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I. *On Striations, the Cathode Dark Space, and the Negative Glow in the Electric Discharge.* By Sir J. J. Thomson, O.M., F.R.S.*

Summary.

When an electric discharge passes through a gas electrons are lost by combination with positive ions or uncharged molecules, or by diffusions to the walls of the vessel in which the gas is contained. In a steady discharge these losses must be balanced by the production of free electrons; if these are liberated by the collisions made by other electrons the latter must get from the electric field the energy required for the ionization. The stable form of the discharge will be that which produces the requisite number of electrons with the least expenditure of energy, for then the current through the gas will be maintained by a minimum difference of potential. When an electron ionizes by collision the whole of the energy given to it is not utilized in ionization. For besides the collisions which ionize it makes inelastic resonance collisions; these consume energy which, as far as ionization is concerned, is wasted. Thus in producing an electron by collision more energy than that measured by the ionizing potential of the gas must be expended. If for every ionizing collision made by an electron it makes, on the

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* Communicated by the Author.

average, β inelastic resonance collisions, the average energy spent in producing an electron is

$$V_0+\beta R,$$

where V_0 and R are the ionizing and resonance potentials respectively. The value of β will depend upon the velocity of the colliding electrons, for we know that the probability of an electron detaching an electron by collision with a molecule is very small when the energy of the electron is only just greater than the ionizing potential and increases to a maximum when the energy of the electron is between 150 and 200 volts. Little is known about the variation of the probability of an inelastic resonance collision with the energy of the electron, but what evidence we have points to the conclusion that the probability is a maximum at the resonance potential and diminishes as the energy of the electron increases. Each of these effects will make β diminish as the energy of the electron increases, so that electrons can be produced more economically by fast electrons than by slow ones. If this is so, then to produce electrons with the least expenditure of energy the electric force acting on the electron ought to be very large at the beginning of its path so as to raise its energy well above the ionizing potential. After this the force may drop to a small value and the energy already acquired by the electron be spent in producing ionization. This will absorb less energy than if the force is kept constant and the energy of the electron maintained at a uniform value just above the ionizing potential. The distribution of the force in the first of these cases is that in the striated discharge, in the second that in the uniform, positive column. To produce a given number of electrons the arrangement in the striated discharge is the most economical, but the striated arrangement may involve a greater loss of electrons by recombination and diffusion than the uniform column, and the theory of stratification advanced in this paper is that the discharge is stratified or not according as the economy in producing a single electron by the stratified arrangement is not or is overbalanced by the increased number of electrons which have to be produced.

The basis of this explanation is that whereas an increase in the energy of the electron increases, within certain limits, its chance of producing ionization by collision; the chance of its making a resonance collision has a sharp maximum at a particular energy and diminishes rapidly on either side of this maximum. This principle has important applications to the theory of the cathode dark space and the negative glow as well as of the positive column. We may express it by saying that it is only when the energy of the electron is between R and $R+\Delta R$ that its collisions excite luminosity. Consider, first, the cathode dark space; the wide range in velocity of the positive rays coming from this space indicate that ionization is taking place throughout its length. There is a strong electric field in the dark space, and when an electron is liberated it will acquire energy rapidly. Regarded as a producer of resonance radiation the electron is active only when its energy is between R and $R+\Delta R$, the distance in which it is active is where it is acquiring the energy ΔR, and the length of this is $\Delta R/Xe$, where X is the electric force at the point in the dark space where the electron has acquired energy equal to R. Thus the length of its effective path, and therefore the probability that it makes a light-giving collision, is inversely proportional to X. According to Aston's measurements X is proportional to the distance from the boundary of the dark space; thus the brightness of the luminosity excited by these electrons will vary inversely as this distance, so that the luminosity will have a very well-marked maximum at the boundary. Those electrons which cross the boundary with energies between the given limits, will, since the electric force is exceedingly small in the negative glow, remain in the active state during the whole of their path through the negative glow, and thus a very large proportion of them will produce luminous radiation. They will not, however, ionize the gas. The ionization in the negative glow will be due to electrons which cross the boundary with energy greater than V_0, the ionizing potential. The energy of the electrons crossing the boundary will range from that corresponding to the full cathode fall of potential for those which have started from the cathode itself to very small values for those which come from near the boundary. All with energy greater than the ionizing potential will ionize and lose their energy as they pass through the gas. Those with energies in the neighbourhood of the maximum ionizing potential will do so most quickly, the electrons with these intermediate energies will be absorbed more rapidly than the very fast or very slow ones, and the ionizing power of the stream will diminish rapidly at first, more slowly afterwards as the distance from the boundary increases. The proportion of very fast and very slow electrons will increase with this distance, the slow group will lose more by diffusion to the sides of the discharge-tube than the fast one, so that ultimately the stream will be reduced to high-speed cathode rays of small ionizing power. This agrees with observation, for these rays may often be seen passing not only through the negative glow but through the positive column and striations.

Though the energy of most of the electrons when they cross the boundary of the dark space is too large for resonance collision, yet, as they lose energy by ionizing collisions, they may reach a stage where their energy is between R and $R+\Delta R$, and then they will produce luminosity.

Since the electric force in the negative glow is exceedingly small, the electrons and positive ions liberated by ionization will accumulate until their density is great enough to carry the current by diffusion. The gradient in the negative glow both for electrons and positive ions will be a diminution in density as the distance from the boundary of the dark space increases. In addition to this gradient there will be an exceedingly steep one at the boundary itself. The diffusion of electrons into the dark space is prevented by the electric field, which stops them when they cross the boundary; the diffusion of positive ions into the dark space is, on the other hand, promoted by this field.

IN the steady state of the positive column work must be done by the electric field to

(1) Ionize the gas at a rate sufficient to replenish the loss of electrons due (α) to recombination with positive ions, (β) to their attachment to uncharged molecules, and (γ) to their diffusion to the walls of the discharge-tube.

(2) To supply the energy lost in those inelastic collisions which, though they put the molecule in an "excited" state and absorb energy proportional to the resonance potential, do not produce ionization. The energy absorbed in this way may under certain conditions be considerable in comparison with that spent on ionization. When an electron has acquired energy greater than that measured by V_0, the ionizing potential of the gas through which it is passing, it can produce ions by collision. The chance that it produces an ion in going through a distance dx may be written in the form $\phi(V)dx$, where V is the energy of the electron and ϕ a function which involves the pressure of the gas. In the same distance it is liable to make an inelastic collision, which will absorb an amount of energy R_1; the chance that it does this we shall denote by $\Psi(V)dx$. Thus in going through a

distance d the chance that the electron makes an ionizing collision is

$$\int_0^d \phi(V)\,dx.$$

The chance that it makes a resonance one is

$$\int_0^d \Psi(V)\,dx,$$

the energy absorbed is

$$V_0\int_0^d \phi(V)\,dx + R\int_0^d \Psi(V)\,dx,$$

and the number of ions produced

$$\int_0^d \phi(V)\,dx\;;$$

hence the energy absorbed in producing an ion is

$$V_0 + R\frac{\int_0^d \Psi(V)\,dx}{\int_0^d \phi(V)\,dx},$$

say

$$V_0 + \beta R.$$

The potential difference in the distance d will be proportional to the product of $V_0+\beta R$ and f the fraction of the electrons lost in travelling through a distance d.

There is evidence that in many cases the second term βR is larger than the first, and that the energy of electrons moving through a gas is to a large extent frittered away on non-ionizing effects, so that any saving in these would reduce considerably the energy required to produce an ion. Lehmann (Proc. Roy. Soc. cxv. p. 624, 1927) has shown that in nitrogen the ionization produced by electrons with energies of 200 volts or over only accounts for about 30 per cent. of the energy given up by the electrons to the gas, so that in this case the term βR must be more than twice V_0.

Energies corresponding to 200 volts are much larger than those we have to do with in ordinary striations, but we shall see that the slower electrons might be expected to convert a still smaller proportion of their energy into ionization.

It seems well established that the chance of an electron ionizing by collision is very small when its energy is but a little greater than the ionizing potential, and that the chance increases as the energy increases until the energy is of the order of 150 or 200 volts, after which the probability of ionization diminishes as the energy increases (see Kossel, *Ann. der Phys.* xxxvii. p. 393, 1912). Thus $\phi(\mathrm{V})=0$ until $\mathrm{V}=\mathrm{V}_0$, it at first increases rapidly with $\mathrm{V}-\mathrm{V}_0$, attains a maximum when $\mathrm{V}-\mathrm{V}_0$ is between 150 or 200 volts, after which it diminishes.

The probability of an electron making an inelastic resonance collision seems (see K. T. Compton and F. L. Mohler, Bulletin of the National Research Council, vol. 9, p. 52, 1924) to be a maximum when the energy of the electron is equal to the resonance potential and to diminish as the energy increases.

The information we possess as to the way the probability of inelastic resonance and other non-ionizing collisions varies with the energy of the electron is exceedingly meagre; the experiments on resonance collisions seem to have been almost entirely confined to measurements of the resonance potentials and tell little, if anything, about their probability. That this diminishes as the energy of the electron diminishes is confirmed by the fact that, in some cases of the electrodeless discharge where the speed of the electrons is high, we get very intense ionization with little or no visible light. If we knew the form of the functions $\phi(\mathrm{V})$ and $\psi(\mathrm{V})$, we could calculate the value of

$$\frac{\int_0^d \Psi(\mathrm{V})dx}{\int_0^d \phi\,(\mathrm{V})dx}$$

for any assigned distribution of the electric force in a striation of length d and could compare it with that for the same length of the uniform positive column. Let f be the fraction of electron lost in passing through a distance d, then f is the number of electrons which an electron must produce in passing through a striation, and the energy required to produce this number of electrons is

$$f\left(\mathrm{V}_0+\mathrm{R}\frac{\int_0^d \Psi(\mathrm{V})dx}{\int_0^d \phi\,(\mathrm{V})dx}\right), \quad . \quad . \quad . \quad . \quad (1)$$

and this is the fall of potential in the striation required to give this energy to the electron. The criterion which determines the type of discharge is that the expression (1) should be a minimum, for this would make the potential difference required to maintain a given current a minimum.

In certain cases a correction which will be additive will be required for (1), for this expresses the condition that the energy given by the electric field to the electrons is sufficient to produce as many electrons as are lost. The electrons which are lost may, however, not only be abstracted from the gas, they may carry energy along with them. Thus, for example, if those which diffuse to the walls of the vessel have a finite amount of energy when they reach the walls their loss is not only a loss of electrons but a loss of energy as well, and this loss must be made good by the electric field, this will raise the potential difference in the striation beyond the value given by (1).

We have seen reasons for believing that β (p. 2) will be smaller for fast electrons than for slow, so that, in a sense, high-speed electrons (if their energy is not greater than 200 volts) are more economical ionizers than slower ones. We see from the form of expression (1) that its value will depend upon the value of V and the way V is distributed through the striation. The distribution of V would be known if we knew the distribution of the electric force along the striation. The theory of striation proposed in this paper is that, in consequence of the way the loss of energy by inelastic resonance collisions depends upon the energy of the electron, it is possible to have a non-uniform distribution of electric force through the striation which makes (1), and therefore the potential difference in the striation, less than it is for the uniform positive column. When this is the case the discharge will be striated. On this view stratification occurs because the distribution of force in the stratified discharge makes the energy wasted in non-ionizing collisions less than it would be if the electric force were uniform.

A gas which had no resonance potential less than the ionizing potential or, at any rate, no way of absorbing energy except by being ionized, would not on this view be striated.

In the uniform positive column the electric force is constant along the column, while in the striated discharge the force varies from point to point. The nature of this variation will be determined by the following considerations:— The positive column is on the anode side of the negative glow and is separated from it by the Faraday dark space. In the negative glow the electric force is exceedingly small, and, though there is intense ionization, the energy required for this comes mainly from cathode rays starting from the cathode and the dark space, and has not to be supplied by processes in the negative glow itself; this external energy is exhausted at the end of the negative glow. To produce ionization beyond this glow an electric field must be built up between the glow and the anode. The density of the electrons in the negative glow is very great, and from the anode end of it a slow stream of these sufficient to carry the current emerges. This will produce an excess of negative electricity in the region beyond the end of the glow, and this will make the electric force increase as the distance from the end increases. The rise of V with this distance x is given by the space-charge formula

$$\mathrm{V}=\left(9\pi i\sqrt{\frac{m}{2e}}\right)^{\frac{2}{3}}x^{\frac{4}{3}}, \qquad . \quad . \quad . \quad . \quad (2)$$

where i is the density of the current and m and e respectively the mass and charge of an electron. Until x is great enough to make V equal to the resonance potential the electron will not be able to excite luminosity and the discharge will be dark. This dark interval corresponds to the Faraday dark space. When x is greater than this value there will be luminosity but at first no ionization, and as no positive ions are produced to balance the negative charge carried by the electrons the electric force will go on increasing with x. In fact, the absorption of energy by the inelastic resonance collisions will make V increase more rapidly with x than it would if it continued to be represented by equation (2). When V reaches the value of the ionizing potential ionization will set in, and, though an electron is produced along with each positive ion, the electrons move away so much more rapidly from the place of ionization than the positive ions that the latter will accumulate, and the net result will be the production of a positive charge at the place of ionization. This will diminish the excess of negative electricity over positive and so slow down the rate of increase of X (the electric force) with x. X, however, will continue to increase for a time, and more and more positive ions will be produced as x increases until a point is reached when the positive charge balances the negative and the density of the electrification vanishes; beyond this the electrification will be positive and the electric force will diminish as x increases, the diminution may go on until there is not enough energy in the electric field to produce ionization. Then the ionization, as in the negative glow, will be produced by electrons which have acquired their energy before they arrive at the place where they ionize. Just as in the negative glow these electrons will lose their energy after going through a certain distance, the glow will then come to an end and a new Faraday dark space will begin and the cycle of changes we have just described will recur. The changes in the electric force in this cycle are represented in fig. 1, where the ordinates represent the electric force at P and the abscissæ the distance of P from the beginning of the Faraday dark space. The potentia difference between O and P is represented in fig. 2 by the continuous lines for the striated discharge and by the dotted

Fig. 1.

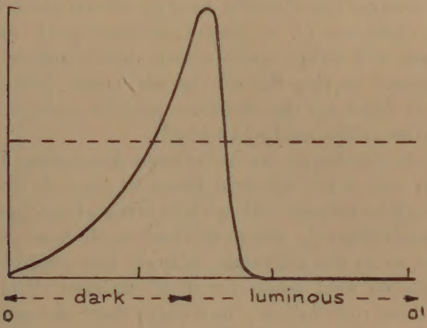
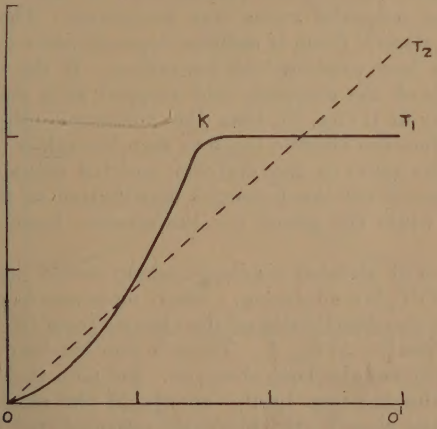


Fig. 2.



one for the uniform column. The column will be striated if T_1 is below T_2.

In the uniform column the electric force is constant throughout and just sufficient to supply at each point enough energy to balance the local loss of electrons. In the striated discharge the kinetic energy of an electron at the head of a striation (*i. e.*, the luminous part nearest the cathode) rises to a value much above that required to supply the local losses; in the tail of the striation, however, little or no work is done on the electron and its energy sinks to a very low value at the end of the tail.

The striated discharge we have been discussing is one of a special type where the electric force in part of the striation falls to negligible values. If with this distribution of electric force the ionization is accomplished with less expenditure of energy than in the uniform column the uniform column will be unstable and some form of striated discharge will occur. It does not follow, however, that the special form of striated discharge we have discussed is the most economical of all possible forms; there are many forms of striated discharge intermediate between the one we have considered and the uniform positive column. For example, we have supposed that the energy of the electron was increased to such an extent that the electric force fell to zero and no further work was done on the electron, so that the portion KT_1 of the potential curve was horizontal. The extent to which the electric force is reduced depends upon the number of positive ions produced by ionization. If the increase in the energy of the electrons had stopped at a stage earlier than K, say at L (fig. 3), then the ionization might not be able to reduce the electric force to zero, though it can reduce it below the value in the uniform positive column; in this case the graph for the potential distribution is that shown in fig. 3, while the graph for the electric force is that in fig. 4.

The form of striated discharge which would occur is that for which $O'T_3$ is a minimum. Many observers have obtained graphs for the distribution of the electric form in the striated discharge similar to fig. 4. There is another form of distribution which has also been observed. Suppose that, instead of stopping the increase in the energy of the electron at an earlier stage than K, the increase is carried still further, so that the electron produces so much ionization that the electric force instead of vanishing becomes negative in the tail of the stria, the electron while moving against this force will restore to the electric field some of the energy it had received from it while passing through the head of the stria. The graph for the electric force in this case is of the type shown in fig. 5, while that for the potential is given in fig. 6.

In the Phil. Mag. (xviii. p. 441, 1909) I described experiments which showed that under certain conditions striations were produced in which the electric force near the tails of the striæ was in the opposite direction to that at the head.

Fig. 3.

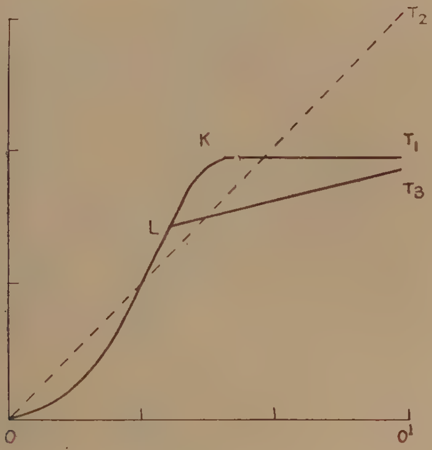
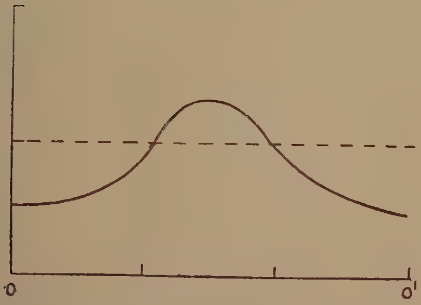


Fig. 4.



The mathematical theory of the passage of electricity through a gas in which ionization is being produced by collisions between molecules and electrons is very complex, as the following discussion of the simplest case of all, that of the uniform positive column, will show. In the steady state electrons have to be produced by collisions to replenish the losses due to combination of electrons with molecules and positive ions and by diffusion to the walls of the discharge-tube.

Fig. 5.

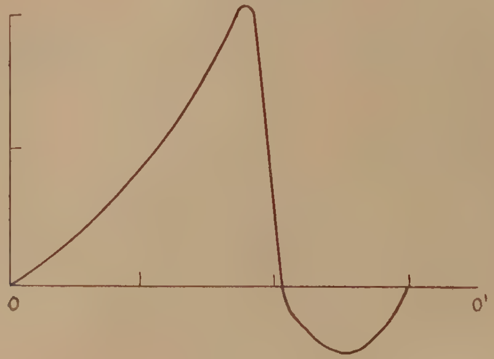
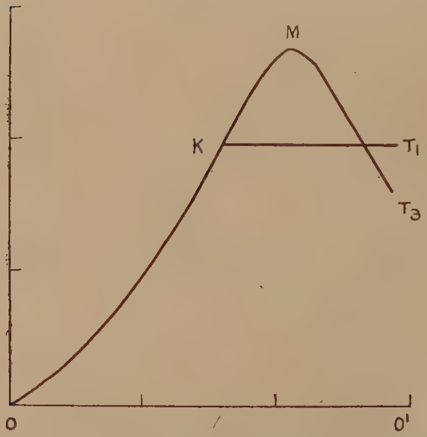


Fig. 6.



In most gases we should expect the losses due to the combination of electrons with uncharged molecules to be greater than that due to combination with positive ions. For unless the current density is very great, the number of uncharged molecules will be very large indeed compared with that of positive ions. Loeb has measured the number of collisions an electron makes on an average with uncharged molecules before it is captured and forms a negative ion. This number is practically infinite for the inert gases, but falls to a few thousand for strongly electronegative elements; it does not depend upon the density of the gas.

Since the electron is deflected at each collision, its path through the gas is a zig-zag and not a straight line, and the distance measured in the direction of the electric force is only a small fraction of the whole distance travelled.

Very little is known about the direct combination of electrons and positive ions, or whether it takes place at all without the formation of a negative ion as an intermediate stage.

The number of electrons combining with molecules in a slab of unit area and thickness δx in the time δt will be proportional to $n\delta x\delta t \times$ (velocity of the electrons); n being the density of the electrons. If the velocity of the electron due to the applied force is greater compared with that due to thermal agitation, we may take the velocity of the electron as equal to u, the velocity due to the impressed force. And then the loss by union with uncharged molecules will be

$$g_1 nu \,.\, \delta x \,.\, \delta t,$$

where g_1 is a quantity proportional to the pressure of the gas. In addition to the loss by combination, the electrons will be deflected by the collision, and some of them may strike against the walls of the discharge-tube; we shall suppose the loss from this cause to be $g_2 nu\, \delta x \,.\, \delta t$, where g_2 is a constant depending on the radius of the discharge-tube.

Then, if there is no ionization,

$$\frac{dn}{dt} = -\frac{d}{dx}(nu) - gnu,$$

where
$$g = g_1 + g_2,$$

when things are in a steady state,

$$\frac{d}{dx} nu = -gun,$$

or
$$nu = \mathrm{C}\epsilon^{-gx}.$$

Thus a stream of electrons which has a flux equal to unity at its source will, after passing through a distance x, have a flux ϵ^{-gx}. Let us now consider a uniform column in which there is ionization; the electrons at any point in the discharge must have a wide range of velocities. Some of them have been liberated close to the point and will only have acquired a small amount of energy from the electric field; others will have been liberated further away and will have had room to acquire a larger amount of energy. We proceed to find an expression for the number of electrons which possess energy between certain limits. We shall suppose that the collisions made by an electron are elastic, *i.e.*, do not involve an appreciable loss of energy, unless the energy of the electron is great enough either to put the molecule in an excited state or ionize it.

Suppose the rate of ionization throughout the positive column is q. Then the ionization between points distant ξ and $\xi + d\xi$ from P, the place of observation, will be $qd\xi$. The flux due to this will, when the electrons liberated reach P, be reduced to $qd\xi\epsilon^{-g\xi}$. This flux is equal to the number of electrons per unit volume moving in it multiplied by their velocity. If T is the kinetic energy of these electrons their velocity will be $\sqrt{2\mathrm{T}/m}$, where m is the mass of an electron. Hence the density of these electrons at P will be

$$qd\xi\frac{\epsilon^{-g\xi}}{\sqrt{2\mathrm{T}/m}}.$$

If X is the electric force, T the energy of an electron coming from a distance ξ is given by the equation

$$\mathrm{T} = \mathrm{X}e\xi\,;$$

hence $d\mathrm{T}$, the range of energy among the electrons, is equal to $\mathrm{X}ed\xi$.

Thus the density of the electrons at P is equal to

$$q\frac{d\mathrm{T}}{\mathrm{X}e}\frac{\epsilon^{-g\frac{\mathrm{T}}{\mathrm{X}e}}}{\sqrt{2\mathrm{T}/m}}.$$

This expresses the distribution of energy among the electrons whose energy is not so great as the first resonance potential. When the electrons before arriving at P acquire energy greater than this, they may lose energy by inelastic collisions and the equation

$$\mathrm{T} = \mathrm{X}\epsilon\xi$$

will no longer hold. When ξ is $>$ R/X, where R is the resonance potential, the electron may lose energy as it moves through the distance $\xi-\mathrm{R}/\mathrm{X}$. The calculation of the probable loss of energy in this distance would require a knowledge of how the probability of the collision varied with the energy; we have not this knowledge.

There are some indications that the frequency of the resonance collisions has a sharp maximum when the energy of the electrons is equal to the resonance potential, and falls away rapidly as the energy increases. As a working hypothesis, we shall suppose that the chance of an electron making a resonance collision is constant between the range of Re and R′e of the energy where R−R′ is small compared with R, and that outside this range there is no loss of energy by resonance collisions. The distance the electron would move through with energy between these limits is (R′−R)/X; hence the probability of the electron making a resonance collision in its path will be equal to $\alpha(\mathrm{R}'-\mathrm{R})/\mathrm{X}$ when α is constant. The loss of energy at such a collision is R, hence we may put

$$\mathrm{T} = \mathrm{X}e\xi - \frac{a}{\mathrm{X}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

where a is written for $\alpha(\mathrm{R}'-\mathrm{R})\mathrm{R}$.

The law of distribution is, when expressed in terms of ξ,

$$q\frac{d\xi\epsilon^{-g\xi}}{\sqrt{2\mathrm{T}/m}}.$$

Substituting for ξ in terms of T from (3), the law where T > R becomes

$$q\epsilon^{-\frac{ga}{\mathrm{X}^2e}}\cdot\frac{\epsilon^{-\frac{g\mathrm{T}}{\mathrm{X}e}}}{\sqrt{2\mathrm{T}/m}}\,d\mathrm{T}.$$

This, like the preceding, is of the form $\mathrm{A}\frac{\epsilon^{-k\mathrm{T}}}{\sqrt{\mathrm{T}}}\cdot d\mathrm{T}$, but A has different values in the two cases.

This expression (3) will hold until the energy of the electrons reaching P equals that corresponding to the ionizing potential V; when the energy exceeds this value the electrons will lose energy by ionizing collisions. The experiments on this point show that the chance of such a collision increases with the excess of the energy over the ionizing potential, and attains a maximum when the energy of the electron is about that corresponding to a fall through 200 volts. When the energy is not much greater than the ionizing potential, the chance may be taken to be proportional to the excess of energy over the ionizing potential. When this is so, the chance of an ionizing collision in a distance $d\eta$

after the electron has moved through a distance η may be written as

$$\mu(\mathrm{T}-\mathrm{V}e)\,d\eta,$$

where T is the kinetic energy at the place η, and μ a constant proportional to the pressure of the gas.

The loss of energy at a collision is Ve; hence the probable loss of energy in $d\eta$ is

$$\mu(\mathrm{T}-\mathrm{V}e)\mathrm{V}e\,d\eta\,;$$

thus

$$\frac{d\mathrm{T}}{d\eta}=\mathrm{X}e-\mu(\mathrm{T}-\mathrm{V}e)\mathrm{V}e,$$

or

$$\mathrm{T}-\mathrm{V}e=\frac{\mathrm{X}}{\mu\mathrm{V}}\left(1-\epsilon^{-\mu\mathrm{V}e\eta}\right)$$

if $\eta=0$ when $\mathrm{T}-\mathrm{V}e=0$.

If x is the distance the electron has travelled before arriving at $\eta=0$,

$$\mathrm{V}e=\mathrm{X}ex-\frac{a}{\mathrm{X}};$$

hence, when the electron is produced at a distance ξ from P, when T is $>\mathrm{V}e$,

$$\mathrm{T}=\mathrm{V}e+\frac{\mathrm{X}}{\mu\mathrm{V}}\left(1-\epsilon^{-\mu\mathrm{V}e\left(\xi-\frac{(\mathrm{V}+a/\mathrm{X}e)}{\mathrm{X}}\right)}\right)\quad . \quad . \quad (4)$$

and this expression holds from

$$\xi=\frac{\mathrm{V}+a/\mathrm{X}e}{\mathrm{X}}\quad\text{to}\quad\xi=\infty\,.$$

The law of distribution expressed in terms of ξ is

$$q\,d\xi\frac{\epsilon^{-g\xi}}{\sqrt{2\mathrm{T}/m}}.$$

Substituting the value of T in terms of ξ from (4), this expression gives the law of distribution in terms of ξ, and, knowing the value of ξ, we can get T from equation (4).

Thus in the positive column of gas there will, when there is only one resonance potential R, be three types of electrons, each with a special law of distribution :—

1. Slow electrons, whose energy is less than Re.
2. The intermediate electrons, whose energy is between Re and Ve.
3. The fast electrons, whose energy is greater than Ve.

The current sent through unit area by the electrons liberated between ξ and $\xi+d\xi$ is $q\epsilon^{-g\xi}\,d\xi$; hence the current density i is given by

$$i=\int_0^\infty q\epsilon^{-g\xi}d\xi,$$

$$=\frac{q}{g},$$

or $ig=q$; this is the condition that the number of electrons produced by ionization is equal to the number lost. We have supposed that the chance of an electron producing another electron in distance $d\xi$ is $\mu(\mathrm{T}-\mathrm{V}e)d\xi$. If there are $n_{\mathrm{T}}dt$ electrons with energy between T and $\mathrm{T}+\delta\mathrm{T}$ the number of electrons they produce in unit volume per unit time $=\mu(\mathrm{T}-\mathrm{V}e)n_{\mathrm{T}}d\mathrm{T}\times v$, where $v=\sqrt{2\mathrm{T}/m}$, and therefore

$$q=\int\mu(\mathrm{T}-\mathrm{V}e)vn_{\mathrm{T}}d\mathrm{T}.$$

Changing the variable from T to ξ, this is equal to

$$\mu\int_{\frac{\mathrm{V}+a/\mathrm{X}e}{\mathrm{X}}}^{\infty}q\epsilon^{-g\xi}(\mathrm{T}-\mathrm{V}e)\,d\xi.$$

Substituting the value of $\mathrm{T}-\mathrm{V}e$ from equation (4) and integrating, we get

$$q=q\epsilon^{-g\frac{(\mathrm{V}+a/\mathrm{X}e)}{\mathrm{X}}}\frac{\mathrm{X}}{\mathrm{V}}\left(\frac{1}{g}-\frac{1}{g+\mu e\mathrm{V}}\right),$$

or
$$\mathrm{X}\epsilon^{-g\frac{(\mathrm{V}+a/\mathrm{X}e)}{\mathrm{X}}}=g\frac{(g+\mu e\mathrm{V})}{\mu e},$$

an equation to determine X, the force in the positive column.

Writing θ for $g\mathrm{V}/\mathrm{X}$, this equation may be written

$$\theta\,.\,\epsilon^{\theta}=\frac{\mu\mathrm{V}e}{g+\mu e\mathrm{V}}\epsilon^{-\frac{a\theta^2}{g\mathrm{V}^2e}}. \quad . \quad . \quad . \quad . \quad (5)$$

Since $1/g$ measures the distance travelled by an electron before it unites with an uncharged molecule, and $1/\mu\mathrm{V}$ that passed over before its energy falls below the ionizing point, $\mu\mathrm{V}/g$ represents the odds in favour of the electron spending its energy in ionization before being absorbed. When this quantity is large, the greater part of the energy given to the electrons is spent in ionization; when it is small this energy is wasted as far as ionization is concerned.

We see from equation (5) that $\theta\epsilon^{\theta}$ is always less than 1; hence θ must be less than ·56, and hence $X > 1{\cdot}78gV$.

X will approximate closely to $1{\cdot}78gV$ when $\mu V/g$ is large and a so small that the factor $\epsilon^{-a\theta^3/gV^2e}$ does not differ appreciably from unity.

When $\mu V/g$ is small, an approximate value of θ is $\mu Ve/g$, and the corresponding value of X is given by

$$X = \frac{g^2}{\mu e},$$

which is large compared with the previous values.

It is important, especially in connexion with the question of striation, to compare the expression for the force in the uniform column with that for other possible distributions of electric force. We will consider the potential difference required to maintain the discharge between two parallel plates at a distance l apart, when the fall of potential is supposed all to occur quite close to the cathode, and there is no force except in this region.

Let W be the fall of potential close to the cathode, i_0, the stream of electrons coming from the cathode. These electrons will acquire energy equal to We, and will ionize by collision on their way to the anode.

If T is the energy of an electron at a distance x from the cathode, using the same notation as before, we have

$$\frac{dT}{dx} = -\mu(T - Ve)Ve,$$

so that

$$T - Ve = (W - V)e\epsilon^{-\mu Vex}.$$

The stream of electrons at x will be $i_0\epsilon^{-gx}$, and the production of ions between x and $x+dx$,

$$i_0\mu(W - V)e\epsilon^{-\mu Vex}\epsilon^{-gx}dx.$$

Of these only the fraction $\epsilon^{-g(l-x)}$ will reach the anode, so that the stream reaching the anode is

$$i_0\mu(W - V)e\epsilon^{-gl}\int_0^l \epsilon^{-\mu Vex}dx$$
$$= i_0\epsilon^{-gl}\frac{(W-V)}{V}(1-\epsilon^{-\mu Vel}),$$

and as this must equal i_0, we have

$$W = V\frac{(\epsilon^{gl}+1-\epsilon^{-\mu Vel})}{1-\epsilon^{-\mu Vel}}.$$

Thus W is always greater than $V\epsilon^{gl}$.

Let us now compare W with Xl, the potential fall in the uniform positive column in the same distance. First take the case where μVe is large compared with g. Then when $a=0$ we have

$$Xl = 1{\cdot}78 gVl\,;$$

hence

$$\frac{W}{Xl} > \frac{\epsilon^{gl}}{1{\cdot}78\,.\,gl}$$

As the minimum value of ϵ^{gl}/gl is equal to 2·71,

$$\frac{W}{Xl} > \frac{2{\cdot}71}{1{\cdot}78}\,;$$

thus W is greater than Xl, so that to maintain the discharge as a uniform positive column will require a smaller difference of potential than the one with the varying electric field.

Next take the case where μeV is small compared with g. Here

$$Xl = \frac{g^2 l}{\mu e}$$

and

$$W > \frac{V\epsilon^{gl}}{\mu Vel}\,;$$

hence

$$\frac{W}{Xl} > \frac{\epsilon^{gl}}{g^2 l^2}.$$

Now the minimum value of ϵ^x/x^2 is 1·84, so that

$$\frac{W}{Xl} > 1{\cdot}84\,;$$

thus W is again greater than Xl, so that again the discharge will take the form of the uniform positive column rather than that of the varying electric field. We have assumed $a=0$, *i.e.*, that there is no loss of energy by resonance or other non-ionizing collisions. This investigation indicates that in the absence of these the discharge will not be striated.

To find the connexion between X in the uniform positive column and the pressure of the gas we notice that μ is directly proportional to the pressure; g consists of two parts, one depending on the probability of the electron joining on to an uncharged molecule when it passes over unit distance (this will be proportional to the pressure, and will not depend upon the cross-section of the tube); the other part, which measures the loss by diffusion, will depend upon the cross-section of the tube, and will increase as this diminishes. It will also tend to be greater at low pressures than at high. It will not be important in very large tubes, but when the free path of the electron is larger than, or even comparable with, the diameter of the tube, it may well be the predominant term. The quantity denoted by a is directly proportional to the pressure. Thus in tubes of large dimensions, g, μ, and a are all directly proportional to the pressure, and hence from equation (5) X will also be proportional to it. When the diameter of the tube is comparable with the free path of the electron, X will not increase so rapidly as the pressure and, indeed, may decrease as the pressure increases. It will increase as the cross-section of the tube diminishes.

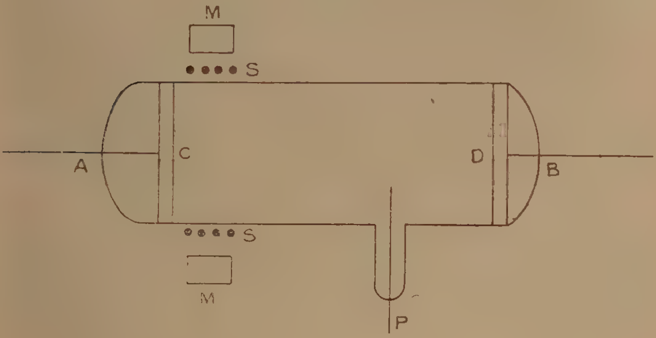
With regard to the effect on X of the current density i, though i does not appear explicitly in equation (5), it may affect the value of the constants g, μ, and a, and thus produce an effect upon X. For example, with large current densities it may not be legitimate to neglect the recombination of the electrons with the positive ions; this recombination will increase the value of g and therefore of X. On the other hand, since the increase in current density increases the luminosity, it may tend to diminish the value of X, as exposure to radiation makes the gas more easily ionized (see J. J. Thomson, Proceedings of Physical Society, xl. p. 79, 1928), and thus diminishes the effective value of V.

When, as in the striated discharge, the electric field is not uniform, the differential equations for the various quantities involved are too complicated to be manageable. We have therefore to fall back on qualitative considerations. In the first place the distribution of electric force in the striations, viz., the very rapid increase in the electric force in front (*i. e.*, on the cathode side) of the luminous part of the striations, followed by the rapid fall to small values in the tail of the luminous portion and in the dark space between the end of this tail and the head of the next striation, is in striking agreement with the results of measurements of the electric force in the striations.

Many years ago (Phil. Mag. (6) xviii. p. 441, 1909) I made a series of experiments in which I used two methods for measuring the force, (1) by probes, (2) by the deflexion of a jet of cathode rays, starting from an electrode contained in a very narrow tube. I have lately made further measurements, using the very simple method represented in fig. 7.

AB is a straight cylindrical tube about 40 cm. long and 3 cm. in diameter. The cathode C and the anode D are flat aluminium disks stretching right across the tube so as to prevent discharges to the back of the electrodes. S is a magnetizing solenoid which serves to keep the cathode rays which start from C parallel to the axis of the tube. P is a platinum wire in a side tube; this is connected with one terminal of an electrometer, the other terminal of which is connected with the anode D; the discharge was produced by a high-tension dynamo which gave up to about 6000 volts. M is an electromagnet, which is used to deflect the cathode rays and shorten the negative glow.

Fig. 7.



With the magnet off the pressure and current through the tube are adjusted until the negative glow reaches, as a uniform column, right up to the anode. A current is sent through the magnet and gradually increased. There is no appreciable change in the potential difference between D and P until the negative glow just fails to reach the anode, and there is a thin dark space between the end of the glow and the anode. Further increase in the current shortens the negative glow and increases the thickness of this dark space; for a time there is no visible luminosity beyond the end of the glow or on the anode itself, and there is a steady increase in the potential difference between P and D; then suddenly a thin sheet of luminous glow appears on the surface of the anode, and this glow gets thicker and thicker as the current through the magnet increases. At first the increase in the thickness is accompanied by a very rapid increase in the potential difference between P and D, but after the thickness has reached a certain value *d* this increase practically ceases, and the potential difference remains constant until the thickness has become much greater than *d*; the glow then breaks away from the anode as a striation, and a dark space is formed between it and the anode. Now the potential difference between P and D begins again to increase, the same cycle is gone through as before, and a second striation is detached. Thus the distribution of potential difference in the striation is that represented by fig. 2.

Very interesting effects occur when a strong electromagnet is placed close to the anode so as to produce a strong magnetic force at right angles to the plane of the paper. This drives the current through the gas against the walls of the discharge-tube; this portion is full of fine striations very near together, the distance between them being only a small fraction of that when the magnetic field is not on: this is what we should expect. The magnetic field has produced a great concentration of the current, and therefore a great increase in the current density. We see from the space charge formula that the distance required to produce a given increase in potential is greatly diminished; the magnetic force produces a great increase in the potential difference between the probe and the anode; under very intense forces the difference of potential between the probe and anode may be greater than that between the probe and the cathode.

On the Length of the Striation.

A striation consists of several parts :—

1. The non-luminous part, where the energy of the electrons is less than the resonance potential.
2. The luminous part, which may be divided into two portions—the head; the part nearer the cathode, in which the electric force is large and the electrons acquire energy greater than the ionizing potential; and the tail, where the electric force is small and the ionization is produced by high-speed electrons coming from the head.

The tail of the striation may be compared with the negative glow, the head with the portion between the negative glow and the cathode, and the non-luminous part to the Faraday dark space. The thickness of the dark layer may be got from the space-charge equation

$$V=\left(9\pi i\sqrt{\frac{m}{2e}}\right)^{\frac{2}{3}} x^{\frac{4}{3}}.$$

If we put in this formula $V=R_1$, where R_1 is the first resonance potential, then x will be the thickness of the dark space. We see from the equation that when V is given ix^2 is constant. Now, in the "normal discharge" i is proportional to p^2, where p is the pressure of the gas. When this is the case px will be constant, so that the thickness of the dark space varies inversely as the pressure. We should expect a similar law to hold for the thickness of the luminous portion at the head of the striation, in which there is no ionization, while in the luminous tail the length of the portion after the electrons have attained their maximum energy will also vary inversely as the pressure, as it will be proportional to the free path of the electron. Where the discharge is not normal the current does not vary as p^2, and the relation between the length of the striation and the pressure will be different.

Relation between the Length of a Striation and the Diameter of the Discharge Tube.

Let us now consider how the distance between striations will vary at different points of a tube of variable cross-section. If a is the radius of any section, i the current density at that section, $i\pi a^2=$constant. Substituting this value of i in the space-charge equation, we find x/a is constant; thus the thickness of the dark space and the length of the luminous head will be proportional to the radius of the cross-section; the length of the luminous tail will also increase with a, because in the smaller parts of the tube the electrons will strike against the walls of the tube sooner than they do in the broader, and hence their path through the gas will be curtailed.

On the view we have taken striations are produced because the waste of energy in non-ionizing collisions is less than it would be if the electric force were uniform. Thus anything which increases the probability of resonance collisions would tend to promote striation. Thus the presence of an impurity with a complicated molecule, or which, under the influence of the discharge, produced a compound with the gas in the tube, would tend to promote striations.

The presence of an electronegative gas would shorten the life of a free electron and thus increase the value of g, and thereby, as equation (5) shows, the magnitude of the electric force required for the discharge. Whether this would favour striation or not would depend upon whether or not the chance of capture of an electron by a neutral molecule diminished as the energy of the electron increased. The energy of the electrons is greater in the striated than in the uniform discharge, and if the increase in energy were accompanied by a diminution in q it would promote striation. Nielsen (Phys. Review, xxvii. p. 716), who made experiments on the attachment of electrons to mercury atoms, found that the relation between the probability of attachment and the energy of the electron is somewhat complicated, for while in general the chance of attachment decreases as the energy increases, there are certain critical values at which the chance is a maximum.

The energy lost at resonance collisions might under certain circumstances be partially restored to the electrons, or it might increase the probability of ionization. For suppose that such a collision puts a molecule into an "excited" state, and that the current density is so great that before this state has disappeared the molecule is hit by another electron: it may, under these conditions, give up to the electron the energy it had absorbed, so that the production of this state would not in the end have absorbed any electronic energy. Again, since it is more easily ionized in the excited than in the normal state, it may be ionized by a collision which in the normal state would have absorbed energy without producing ionization, and thus compensate for the loss of energy incurred when the excited state was produced.

The average interval between two collisions of a molecule with an electron is

$$\frac{1}{N\pi a^2 v}\cdot$$

where N is the number of electrons per c.c., v the velocity of an electron, and a the effective radius of the molecule.

Now $Nve=i$ if i is the density of the current, hence the interval between two collisions is

$$\frac{e}{\pi a^2 i}\cdot$$

If i is a milliampere, $i=10^{-4}$, $e=1{\cdot}6\times10^{-20}$, so that the interval is $1{\cdot}6\times10^{-16}/\pi a^2$. If a is of molecular dimensions, and about 10^{-8}, the interval between the two collisions would be comparable with one second, whereas the duration of the excited state is in normal cases, according to Wien's experiments, of the order of 10^{-7} sec. Thus, though the effects we have been discussing would tend to compensate for the loss of energy in non-ionizing collisions, the compensation with moderate-current densities would in normal gases be so small as to be negligible.

If the energy of a molecule in the excited state were emitted as radiation and then absorbed by an adjacent molecule, which was thereby put into the excited state, and if this process were repeated, the time with which we should have to compare the interval between the collisions of electrons with one molecule would not be the time any particular molecule was in the excited state, but the time which elapses before the process of emission and absorption of a particular quantum ceases. This time might well be greater than 10^{-7} sec., but it were comparable with one second, the quantum at the low pressures in the striated discharge would have travelled to distances from its source far greater than the dimensions of an ordinary discharge tube.

The Cathode Dark Space.

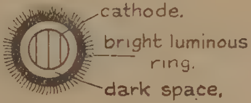
The theory of striation given above is based on the view that the power of an electron to excite resonance radiation by collision diminishes rapidly when the energy of the electron increases beyond the resonance potential. That, in fact, an electron only excites a particular radiation when its energy is within narrow limits. Though little has been done on this point by way of direct experiment, there are indications in the few experiments which have been made which point to this conclusion. A strong reason for thinking that it is true is that it would afford a simple explanation of the cathode dark space and the negative glow. For let us suppose that an electron only excites radiation when its energy is between R and $R+\Delta R$. The range in the velocity of the positive rays which come through the cathode shows that ionization is going on in the cathode dark space. The electrons produced by this will be accelerated in the strong field which exists in that region. Those which are produced near the cathode will acquire high velocities, those starting from near the other end of the dark space only small ones. On the view we are taking, the electron radiates only when its energy is between R and $R+\Delta R$. and thus is only luminous when describing the part of its path when its energy is between these limits. If it is moving in an electric field in which the electric force is X, the length of its path when in this state will be $\Delta R/Xe$, and will thus be inversely proportional to X. The probability of its making a collision when in the active state will be proportional to the length of this path, and this probability is a measure of the intensity of the radiation it emits. Thus the luminosity emitted by an electron in an electric field will vary inversely as the electric force in the field. In the cathode dark space the electric force has been shown by Aston to be proportional to the distance from the boundary of that space, so that the light-producing power of an electron will be inversely proportional to its distance from the boundary, and there will thus be a very great increase in luminosity in that region. Again, consider the electrons which are liberated in the dark space near the boundary, and which, in falling from their place of origin to the boundary, acquire energy corresponding to the few volts which represents the resonance potential. These, when they cross, will have energy between the effective limits; after crossing they get into a region where the electric force is exceedingly small, so that their energy will not change appreciably. They will thus remain in the active state until they make a collision. Thus all the energy they possess will be spent in putting the molecules against which they collide into the excited state. Practically all the energy of these electrons will be spent in producing luminosity, so that in the region just beyond the boundary of the dark space—the negative glow—the luminosity will be very bright. The thickness of the region through which these molecules are active will be measured by the "collision free path" of the electrons. The collision free path is not the ordinary free path calculated from the size of the molecules, but the average distance an electron travels before making a resonance collision. If the gas is a mixture there will be more than one resonance potential—as, indeed, there may be in a pure gas. There may thus be several groups of electrons in the active state, each group being associated with a particular resonance potential. The collision paths of these different groups may be different, so that the thicknesses of the luminous belts just past the boundary of the dark space giving out a particular luminosity may be different, and thus the spectrum of the negative glow may vary with the distance from the boundary (Seeliger, *Ann. d. Phys.* lix. p. 589).

The bright belt of luminosity next the dark space is very conspicuous under suitable conditions. It can easily be shown by using a spherical ball for the cathode, the metal rod carrying the ball being fused into a glass tube, so that only the surface of the ball is exposed to the gas in the discharge tube and takes part in the discharge. When the pressure in the tube is high the discharge starts from only a part of the ball; but on lowering the pressure the discharge will cover the ball, and the appearance will be like that shown in fig. 8. There is next the cathode dark space a belt of luminosity very sharply defined not only on the side abutting on the cathode dark space, but on the other side as well. Stretching beyond this there is fainter luminosity, which gets fainter and fainter as the distance from the ball increases.

In some gases—notably argon—the bright, sharply-defined ring shows different colours; in argon it is red on the outside and yellow on the inside. As the pressure is diminished and the dark space and the rings expand, the glow outside increases in intensity, and the outer boundary of the luminous shell is not so clearly marked; the luminosity outside this shell will, when the pressure is low, fill a large volume.

Since the chance of an electron emitting radiation is proportional to the length of path it has to travel before its energy is increased by a definite amount ΔR, the luminosity due to an electron ought to be increased by a magnetic force at right angles to its path. For under this force the electron would no longer travel along the lines of electric force, but along paths inclined to them at a finite angle; thus the length of path it has to travel to fall through a given difference of electrostatic potential is increased by the magnetic force, and therewith the chance of the electron to excite luminosity. I have made some preliminary experiments on this point, which gave results in accordance with this view. When the pressure was such that with the ball cathode shown in fig. 8 the boundary of the dark space was a concentric sphere, on applying a transverse magnetic field it remained spherical until the force exceeded a certain value depending on the pressure, etc.; in my experiment it was from 50 to 60 gauss. The radius of the luminous boundary continually diminishes as the magnetic force increases; there is little change in the potential fall. This is what would happen if under the magnetic force electrons near the original boundary became luminiferous, while previously they had been dark.

Fig. 8.



The Negative Glow.

We have hitherto only considered the passage across the boundary of the dark space of electrons whose energy was in the neighbourhood of that corresponding to the resonance potential. We shall now consider the faster electrons, which have enough energy to ionize the gas through which they pass. Kossel's (*l.c.*) experiments show that the chance of an electron making an ionizing collision increases from zero when the energy is equal to the ionizing potential to a maximum when the energy is that corresponding to about 200 volts, and after that it decreases rapidly as the energy increases. The energy of the electrons crossing the boundary will range from that corresponding to the cathode fall of potential for those which have started from the cathode itself to very small values for those produced near the boundary. The electrons with energy greater than the ionizing potential will produce ionization and will lose their energy. Those whose energy is in the neighbourhood of the maximum for ionization will do so most quickly, so that the distribution of energy among the electrons will change as they travel through the negative glow. The electrons with intermediate energy will be more rapidly absorbed than either the very fast or the very slow ones, and the ionizing power of the stream will diminish, rapidly at first and more slowly afterwards, as the distance from the boundary increases. Thus the losses by collisions will cause the proportion of very fast or very slow electrons to increase as the stream moves through the gas. The slow ones are more likely to be driven against the walls of the tube by scattering than the fast ones, so that, after passing over a considerable distance, the original stream of electrons will be reduced to a stream of high-speed cathode rays of small ionizing power. This is in accordance with observation, for the high-speed cathode rays can be seen passing not only through the negative glow, but also through the positive column and the striations.

Though when the electrons whose energy when they crossed the boundary was greater than the ionizing potential, and they would therefore not make resonance collisions, yet as they lose their energy by ionizing collisions they may pass into a state in which their energy is between R and $R+dR$, and then they will produce luminosity.

Since the electric force in the negative glow is exceedingly small, the electrons and positive ions liberated by ionization will accumulate until their density is so great that their diffusion is sufficient to carry the current. The densities both of the electrons and positive ions in the negative glow will diminish as the distance from the boundary of the dark space increases, so that their gradient will slope towards the anode. In addition to this there will be an exceedingly steep gradient at the junction of the negative glow and the dark space. The diffusion of electrons into this space is prevented by the electric field, which drives them back as soon as they pass the boundary. On the other hand, the diffusion of the positive ions into the dark space will be promoted by this field, which will move them away from the boundary and thus keep the gradient steep. There will thus be a considerable diffusion of positive ions into the dark space. The diffusion of electrons will be in the opposite direction; these will diffuse from the head of the negative glow—the part next the dark space, where their density is greatest—to the opposite end of the glow, where it is least. The electric current due to their diffusion will be in the same direction as that due to the diffusion of the positive ions.

II. *The Aluminium Electrolytic Condenser. By* R. E. W. Maddison, *B.Sc., Ph.D.(Lond.), of the European Installation Department, International Standard Electric Corporation*.*

INTRODUCTION.

Anodic Polarization.

If the voltage of an electrolytic cell or an electrode immersed in an electrolyte is altered by some cause from its equilibrium value, it is said to be polarized; anodically if it is made more positive than the equilibrium value; cathodically if more negative. Polarization may be produced by impressing an external voltage on the electrodes of the cell; it may result from concentration changes in the electrolyte, or from some interference with the main electrode reaction itself, as for example, the production of a non-conducting film on the electrode surface.

When a metal dissolves anodically, producing metal ions capable of combining with the ions of the electrolyte to give a sparingly soluble substance, further solution of the metal may be hindered as a result of the deposition of a film on the electrode surface. The presence of the film reduces the area of the electrode in contact with the electrolyte, and consequently increases the current density on the parts not affected. An increased polarization is then necessary to maintain a given current, and the electrode reaction may be modified. In those cases where the electrode surface is completely covered by such a film, exceedingly high polarizations may occur.

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* Communicated by Rollo Appleyard.

The physical properties of the film, such as its porosity, thickness, electrical conductivity, and so on, vary in different cases. It is upon the formation of badly conducting films at the surface of a metal anode, permitting the maintenance of high voltages between the electrode and the electrolyte, and preventing the discharge of anions (the passage of any appreciable current), and the relative stability of the anode film when made a cathode that the production of electrolytic condensers and rectifiers is rendered commercially possible.

The characteristic property of the anode film upon which its rectifying property depends is that of unidirectional current conductance. When the electrode is made positive, the current passing is very small after the film has formed ; but on reversing polarity, current conduction is possible. The film, therefore, can act as a valve, and by suitable arrangements of electrodes bearing these films rectification of alternating currents is possible. The film also exhibits a very high electrostatic capacity, which property is utilized for the production of static condensers.

Although this valve action has been observed with most metals under suitable conditions, only two, namely aluminium and tantalum, have gained wide use commercially for rectifiers. For condensers, aluminium alone would appear to have found application.

Theories of Electrolytic Valve Action.

The various theories that have been advanced to explain the unidirectional current-flow characteristic and the dielectric properties of anode films may be divided into two classes :—

1. The Gas Film Theory,
2. The Solid Film Theory,

according as the active layer responsible for the phenomena is considered to be gaseous or solid. Although a visible oxide film is present on a formed anode (*e. g.* aluminium), it is certain that this visible layer is not the active one, but that another inner film is formed that is responsible for the behaviour of the electrode.

1. *The Gas Film Theory.*

K. E. Guthe (7) ascribed the high resistance of the aluminium anode to the presence of a thin film of oxygen gas covering the electrode, preventing the passage of negative ions from the electrolyte to the electrode. He likened the film produced on the electrode surface to a semipermeable membrane, allowing only certain ions to pass through it and to discharge. The behaviour of an ordinary copper ferrocyanide semipermeable membrane was compared with that of an aluminium anode, and found to be similar. It was observed that a high resistance was present when current was passed from a copper to a platinum electrode immersed in an electrolyte, the two electrodes being separated from each other by the semipermeable membrane; in the reverse direction the resistance was very low.

The gas-film theory has been supported in particular by A. Günther-Schulze (23, 24, 28), who considers that during the formation period of the valve metals there are produced simultaneously two films:

(*a*) an inactive solid oxide film,
(*b*) an active gas film.

The solid film is not responsible for the rectifying or condenser properties of the electrode, but serves to hold in position the oxygen gas film, which has the properties of a dielectric. The pores of the oxide layer, in so far as they are not occupied by gas, are filled by electrolyte. Electrons from the metal electrode can cross the gas film, but electrolytic ions from the electrolyte are unable to do so.

In extending Günther-Schulze's hypothesis, A. H. Taylor (33) considers the gas film to be held between an aluminium hydroxide layer and the aluminium electrode: the gas in contact with the aluminium surface combines partially with the metal to give a thin film of aluminium oxide.

2. *The Solid Film Theory.*

The rectifying and condenser properties of the aluminium anode have been ascribed by other workers (11, 14, 16, 34, 37, 38) to the presence of a solid film acting as

(*a*) a Wehnelt interrupter,
(*b*) an ohmic resistance,
(*c*) a true dielectric,
(*d*) a semipermeable membrane.

J. Slepian (30), in his contribution to the solid film theory, has applied the principle of thermionic rectification to explain the operation of thin films such as occur in electrolytic and other rectifiers.

He considers the gas film theory of rectification to be untenable on the following grounds. A gas film has a low dielectric constant (a little over unity), so that it is difficult to account for a sufficient lowering of the work function to permit electron emission from a metal surface at ordinary temperatures; the work function for the escape of electrolytic ions from an aqueous solution should be less than in the case of electrons escaping from a metal surface; lastly, electronic conduction may be imparted to the electrolyte without in any way destroying the rectifying properties of the film. He prefers to ascribe the behaviour of a valve anode to the solid film covering the electrode surface. In the case of aluminium the film is thought to consist of a transition or dehydration product of aluminium hydroxide produced during the forming period. This film has insulating properties in consequence of the almost complete lack of free electrons, exactly as in the case of a vacuum. Electron emission from the metal electrode into the insulating film is controlled by a work function as in the case from a metal to a vacuum. As a result of the definite time required for electrons to traverse the film from one electrode to the other, space-charge effects may arise, and thereby reduce the current flow to a very small value.

The dielectric constant of the film will also influence the work function. The extent of the attraction exerted by the dielectric on the electrons escaping from the metal surface will depend on whether the work function forces are operative within or without the dielectric layer. Assuming a dielectric constant of 13, the work function may be reduced to from 1/13 to 1/7 of its value for vacuum. In view of the fact that the electron emission is approximately proportional to the work function, it follows that it is possible for electron emission to take place at ordinary temperatures into a film of dielectric constant ca. 13, and that the electric field necessary to enable electrons to overcome the work function will be correspondingly reduced.

The above outline has assumed a uniform distribution of the dielectric film over the surface of the electrode. Seeing that the forces of the work function are operative through a distance of ca. 10^{-8} cm., which is of the order of atomic dimensions, this would mean that the film is discontinuous. It is possible that even in the case where the film is formed or built up on the electrode itself, the work function is suppressed at some points and is operative at others: electrons will pass from the metal to the film only at certain discrete points. By combining a favourably polarizable junction surface with one that is non-polarizable, we obtain an asymmetric arrangement which will exhibit the unidirectional current flow characteristic upon which the production of electrolytic rectifiers and condensers is dependent.

F. M. Gentry (6) has established mathematically that the electronic conduction in unidirectional current conducting non-metallic films follows essentially the same law as that found for electronic conduction in an evacuated space. Satisfactory agreement was obtained between calculated and observed values for the current passed at various voltages by the film of an aluminium electrolytic condenser (see pp. 228 and 230 of discussion to (29)).

In connexion with the solid layer theory, it is interesting to note that a condenser with a solid dielectric (calcium fluoride), and analogous to the electrolytic type of condenser, has been prepared (18). A metal filament covered with a layer of the salt is fused into a glass vessel, the walls of which are locally covered with a metal coating. The vessel is highly evacuated, the filament is heated to vaporize the salt layer, and finally the filament is heated to a higher temperature in order to volatilize it and deposit it on the salt layer. The dielectric is 100–150 molecules thick, and has a breakdown voltage of ca. 10^8 V./cm. Particulars of the capacity of this condenser, as well as other electrical properties, do not appear to be available.

W. W. Taylor and T. K. H. Inglis (34) found that the essential peculiarities of an aluminium anode could be reproduced by means of a platinum anode having a film of aluminium hydroxide deposited upon it. This film acts as a semipermeable membrane in permitting the diffusion through it of certain salts, but not others (*v. infra*). A. Rouban (22) followed up this work, using a copper ferrocyanide semipermeable membrane (*cf.* Guthe *supra*; see also (35)).

It may be mentioned that A. L. Fitch (5) proposed the theory of a double dielectric, consisting of a gas and a solid layer, to account for the behaviour of the aluminium anode.

Formation of the Anode Film.

In considering the various experimental data, reference will be made almost entirely to aluminium, and occasionally to tantalum, as it is these metals that have been most studied in connexion with their use for rectifiers and condensers.

When one of the so-called valve metals is made an anode in an electrolyte, the voltage necessary to maintain a given current density increases almost proportionally with the time of closed circuit. At a certain voltage partial breakdown, and at a still higher voltage complete breakdown, of the film occurs. This period of polarization is referred to as the "formation" period.

Formation of the dielectric film can take place on D.C. or A.C. The film which first appears on aluminium is transparent and colourless, but as its thickness increases, interference colours become visible, and after usage it appears greyish, due to the increased thickness of the film. The current density at a given voltage and frequency has considerable influence on the time of formation of the film. The greater the current density (small surface area) the more rapid the formation. The following figures obtained by H. D. Holler and J. P. Schrodt (9) are of great interest in this connexion. The application of 25 V. D.C. to an area of 1 cm.^{2} of aluminium anode gave almost instant formation, the current being reduced nearly to zero in 3 seconds. With an area of 300 cm.^{2} the formation was so slow that even with an applied voltage of 120 V. D.C. several hours were necessary to effect complete formation. Using A.C. under similar conditions to those just described, the time required for formation was about five times as great. The formation is also influenced by the composition of the electrolyte and the temperature.

Anodically treated aluminium heated *in vacuo* to 1200° C. evolves a negligible amount of gas, from which it is concluded (32) that the anode film consists of aluminium oxide and not hydroxide. This is interesting in connexion with Slepian's theory (*v. supra*) regarding the nature of the active layer.

Thickness of the Active Layer.

It has been mentioned above that a distinction has to be made between the visible oxide layer and the inner active layer. The thickness of the active layer has been determined by measurements of electrostatic capacity (making the assumption that the dielectric constant is unity), by estimation from interference colours exhibited by the film, and by chemical analysis. The last two methods assume that the entire thickness of the film on the electrode is effective as a dielectric. Capacity measurements give results of a different order of magnitude from other methods of determination. (For a summary of the various values see (1)). Capacity measurement gives values of the order of 10^{-6} cm. for aluminium formed at 100 V.: other methods give values of $20–100 \times 10^{-6}$ cm. This discrepancy, and the fact that the thickness determined by capacity measurements is practically independent of the electrolyte, suggests that the film produced on aluminium consists of two layers. According to Günther-Schulze (28), the thickness of the active layer is dependent on

(*a*) the metal employed,
(*b*) the applied voltage;

and is independent of

(*a*) the electrolyte for aqueous solutions,
(*b*) the temperature,
(*c*) the method of formation.

TABLE I.

Voltage.	Relative thickness δ/ϵ.	
	Aluminium.	Tantalum.
50	6·4	4·1
100	10·3	7·1
150	16·1	11·6
200	22·3	17·0
250	29·3	22·9
300	37·1	28·8
350	46·6	34·6
400	58·0	40·3
450	71·0	45·0
500	85·9	49·1

δ = absolute thickness.
ϵ = dielectric constant.

Table I. shows the relative thickness

$$\frac{\text{absolute thickness}}{\text{dielectric thickness}} = \frac{\delta}{\epsilon}$$

of the active layer formed on aluminium and tantalum at various voltages, assuming a dielectric constant of unity. Determinations of the thickness of the active layer depending upon capacity measurements are subject to the effect of frequency (*v. infra*), though at a given frequency the electrostatic capacity is a function of the applied voltage; this capacity is taken as being a measure of the thickness of the active layer.

Resistance of the Active Layer.

The high resistance of the anode film has been ascribed to the development of a counter E.M.F., but the evidence mainly indicates that the resistance is of an ohmic nature. It depends not only on the thickness of the active layer, but also on the applied voltage (26). From the figures given in Table II. it is seen that during the formation period the current flow decreases at a quicker rate than the thickness of the active layer increases, so that the resistance of the active layer at constant voltage with decreasing forming current very rapidly increases. Tantalum was chosen to obtain the results given in Table II., since with

Table II.

Time.	Forming current. i mA.	Cell voltage. e volts.	Thickness of		$\frac{e}{i} = r$ ohms.	$\frac{r}{\delta}$ ohms/μμ.
			Solid layer. μμ.	Active layer, δ. μμ.		
10″......	100	27	113	2·50		
30	100	73	160	3·53		
40	100	101·3	270	6·00	$1{\cdot}01\times10^3$	$0{\cdot}17\times10^3$
55	11	101·3	300	6·62	9·22	1·39
90	4·1	101·3	305	6·74	24·7	3·67
2′	3·1	101·3	307	6·78	32·7	4·82
10	1·16	101·3	325	7·17	87·2	12·2
60	0·54	101·3	335	7·39	188	25·5
260	0·37	101·3	350	7·72	278	36·0
450	0·25	101·3	355	7·82	413	52·8
2880	0·11	101·3	360	7·93	922	116
7340	0·07	101·3	390	8·60	1450	169
8780	0·06	101·3	395	8·72	1582	181

12·5 cm.² tantalum in 0·05 N. KNO_3. Formed at 100 V. D.C.
Temperature 20° C.

this metal results are not obscured by the incomplete insolubility of the metal in the electrolyte, as in the case of aluminium.

The figures for the resistance of the active layer given in Tables II. and III. show that the discharge of an electrolytic condenser takes place slower than it would if it possessed constant ohmic resistance. The time of discharge is greater the greater the period allowed for charging, since e/i is greater, although the corresponding change in the electrostatic capacity (thickness of film) is much less. The figures given in Table III. must be taken as showing the general trend of the voltage-resistance characteristic, since individual values are dependent on the time elapsing between successive readings, and whether increasing or decreasing potentials are being applied (26).

Table III.

Voltage.	Aluminium. $\frac{e}{i}=r$ ohms.	Voltage.	Tantalum. $\frac{e}{i}=r$ ohms.
350	$2{\cdot}2\times10^4$	200	$0{\cdot}21\times10^6$
300	3·8	180	0·52
250	4·0	160	1·10
200	4·0	140	1·88
150	5·3	120	2·40
100	9·5	120	2·94
50	28·0	80	3·80
25	90·0	60	4·28
	*	40	5·00
			†

* 1000 cm.^{2} of aluminium in ammonium borate solution. Formed at 350 V. D.C. (29).

† 12·5 cm.^{2} of tantalum in 0·05 N. borax solution. Formed for one day at 200 V. D.C. (26).

W. R. Mott (16) gives the specific resistance of the film formed on aluminium in phosphate and sulphate solutions as 10×10^{10} ohms/c.c. and $0{\cdot}8\times10^{10}$ ohms/c.c. respectively at 25° C., the resistance decreasing as a logarithmic function of temperature. W. E. Meserve (12) computes the specific resistance of the solid layer to be $3{\cdot}4\times10^{12}$ ohms/c.c., assuming the layer to consist of Al_2O_3.

Table IV. gives figures showing the current-voltage characteristic for a formed aluminium electrode in ammonium borate solution (29). At constant voltage the D.C. leakage of an electrolytic condenser decreases with time. The D.C. leakage of a film subjected to a potential less than the forming voltage is of the order of a microamp./cm.².

TABLE IV.

Voltage. D.C.	Current density. Amp./1000 cm.²
− 6………	0·8
− 5………	0·4
− 4………	0·1
− 2………	—
+ 40………	0·0001
+ 80………	0·0005
+120………	0·0015
+160………	0·003
+200………	0·005
+240………	0·006
+280………	0·007
+320………	0·009

Aluminium formed in ammonium borate solution at 350 V. D.C.

TABLE V.

Temperature. $t°$ C.	mA./cm.². i.	Ohms/cm.².
15……	0·0075	$13·3\times10^6$
30……	0·025	4·0
40……	0·059	1·60
50……	0·186	0·54
60……	0·375	0·27
70……	0·600	0·17
75……	0·757	0·13

Aluminium formed in ammonium borate solution at 105 V. D.C. for 140 hours. Tests at 100 V. D.C.

Schulze (28) gives a figure of $0·15\times10^{-6}$ amp./cm ² for aluminium formed at 110 V. in ammonium borate solution. The leakage current is considerably increased when corrosion of the electrodes takes place, and may increase 20–30 times. The product of corrosion by accumulating between the plates may even cause short circuit by deforming the plates and making them touch. The leakage current increases also with increase of temperature, as shown by the figures given in Table V. (Bairsto and Mercer (1)). The current-temperature curve is an exponential one, $i = A\epsilon^{at}$. For the figures given in Table V. $i = 2{\cdot}04\epsilon^{0{\cdot}085t}$. The constant "A" appears to be independent of the electrolyte, and dependent on the time of formation; "a," on the other hand, appears to be independent of the time of formation, and dependent on the electrolyte: thus

Electrolyte.	Time of formation.	
	8 hours.	140 hours.
Ammonium molybdate ...	$i=3{\cdot}55\epsilon^{0{\cdot}064t}$	$i=2{\cdot}04\epsilon^{0{\cdot}062t}$
Ammonium borate	$i=3{\cdot}55\epsilon^{0{\cdot}085t}$	$i=2{\cdot}04\epsilon^{0{\cdot}085t}$

Dielectric Strength of the Anode Film.

When the voltage across the film exceeds a certain critical value, sparking is observed to take place at the surface. This voltage, according to Schulze (28), is dependent on the valve metal as well as the nature and concentration of the electrolyte employed, but it is independent of the temperature and current density. The maximum voltage that can be maintained across the film depends on the nature and concentration (of free ions) of the electrolyte that is used for forming the film; it is apparently independent of the valve metal, the current density, and the temperature. For the film produced on aluminium in 0·1 N. solutions of various salts, Schulze (25) gives the following figures for the maximum voltage:—

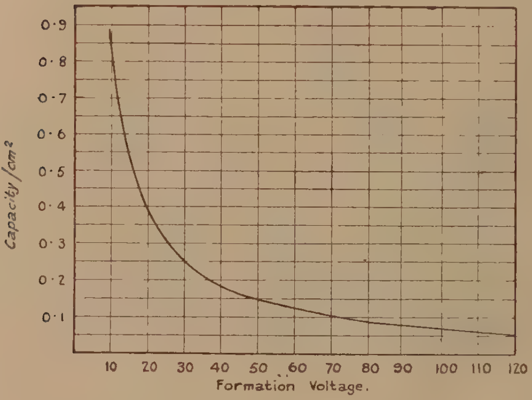
Sodium sulphate	40 V.	Ammonium phosphate ... (? dibasic.)	460 V.
Potassium permanganate .	112		
Ammonium chromate	122	Ammonium citrate	470
Potassium cyanide	295	Borax	480
Ammonium bicarbonate ..	425	Citric acid	536
Sodium silicate	445		

For tantalum in 0·05 N. solutions containing metal free anions (*e.g.* OH', $HCOO'$, C_3H_7COO', H_2PO_4', etc.) the maximum voltage averages about 480 V. (28): the cation, so long as it is not one of a heavy metal, has no influence. The presence of metal in the anions greatly influences the maximum voltage. In 0·05 N. solutions of metal containing anions, tantalum exhibits a maximum voltage of ca. 133 V. for chromium (*e.g.* Cr_2O_7''), ca. 84 V. for iron (*e.g.* $\frac{1}{3}$ $Fe(CN)_6'''$), and ca. 28 V. for platinum (*e.g.* $\frac{1}{2}$ $PtCl_4''$). In the range 0·5–0·05 N. an increase of about 1 per cent. in the dilution of the electrolyte produces an increase of about $\frac{1}{4}$ per cent. in the maximum voltage. At very low concentrations very high values (up to 1900 V.) for the maximum voltage may be reached.

W. R. Mott(16) gives the electric strength of the film formed on aluminium in phosphate solutions as 10^6 V./cm. C. I. Zimmerman(38) gives a slightly higher figure of $5-6\times10^6$ V./cm.

Fig. 1.

Variation of capacity/cm.² with formation voltage.
(Bairsto & Mercer(1)).



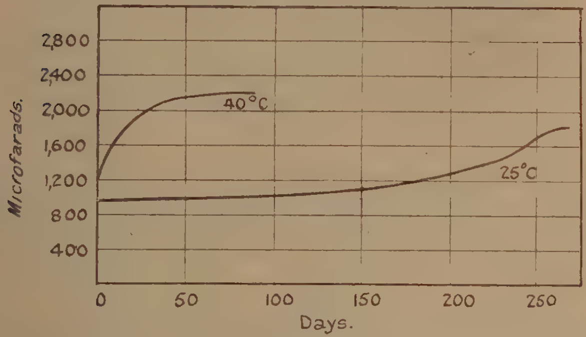
Electrostatic Capacity of the Active Layer.

It has been mentioned above that the thickness of the active layer is determined by capacity measurements. This capacity varies approximately inversely with the potential applied to form the film, and amounts to about 0·7 m.f./cm.² for formation at 10 V. D.C.(26), and 0·18 mF./cm.² at 30 V. D.C.(29) for aluminium. Fig. 1 shows a curve, which averages the results of several workers, giving the relationship between formation voltage and capacity/cm.² for aluminium aqueous electrolytes(1). The rate of growth of the activ layer on an aluminium anode has been investigated by N. A. de Bruyne and R. W. W. Sanderson (2), who found that the reciprocal of the capacity increased to its final steady value approximately logarithmically with time. (See also (1) for a summary of other measurements.)

When the voltage applied to a cell is higher than that at which the film was originally formed, the film adjusts itself to correspond to the new voltage. When there is a large electrode surface in the cell, then this increased voltage may result in a heavy flow of current, which may cause overheating and damage to the cell if the film is not able to adjust itself with sufficient rapidity to the new condition. The insertion of a current limiting device in the circuit will prevent any such damage.

Fig. 2.

The capacity-time change of electrolytic condensers operated at half the formation voltage. Both with ammonium borate solution of same conductivity. Different temperatures. (Siegmund (29).)



Under the reverse condition, where a cell is operated at a voltage lower than the forming voltage, a very slow adjustment to the new conditions takes place. An electrolytic condenser, with continued working, will gradually accommodate itself to the lower voltage ; its capacity will slowly increase on account of electrolytic action on the film reducing its thickness. This rate of change is influenced by the temperature and the conductivity of the electrolyte, being more rapid for high temperatures and conductivities (see figs. 2 and 3). The variation of capacity with temperature appears to be characteristic of the electrolyte (1.

The capacity of an electrolytic condenser decreases with frequency, though many workers seem to have ignored this factor. The change which does occur is greater in condensers with electrolytes of high specific resistance and with films formed at low voltages. The capacity-frequency characteristic of a new aluminium electrolytic condenser and the same unit after a year's continuous service is shown in fig. 4. In this instance the fall in capacity is influenced also by the special shape of the anode plates, which are corrugated.

Fig. 3.

Capacity-time change of electrolytic condensers operated at half the formation voltage. Both at room temperature. Ammonium borate solution of different conductivities. (Siegmund (29).)

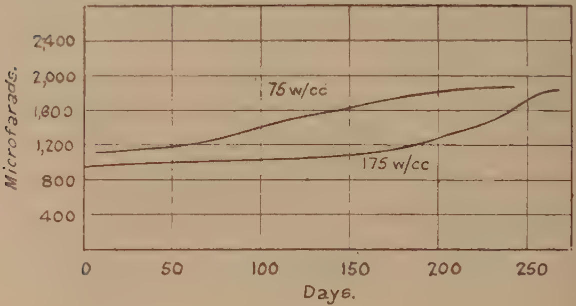
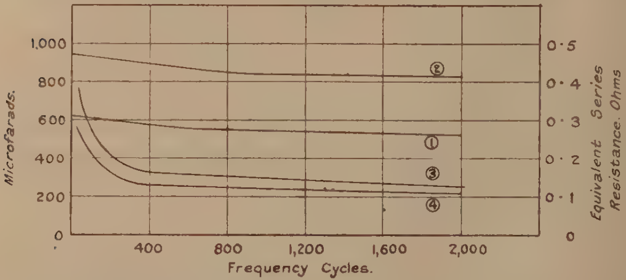


Fig. 4.

Capacity-frequency and resistance-frequency change of aluminium condenser formed at 100 V. and operated at 63 V. D.C. (Siegmund (29)).



(1) Capacity curve. Initial.
(2) Capacity curve after one year's continuous service.
(3) Resistance curve. Initial.
(4) Resistance curve after one year's continuous service.

The Electrodes.

(a) *The Anode.*

The purity of the metal employed as anode in electrolytic condensers and rectifiers has considerable influence on the efficiency, life, and corrosion of the cell.

For rectifying purposes, the copper content of aluminium is of importance. When this is less than 0·05 per cent., the current delivery and the life of the cell fall off rapidly, and when it is over 0·15 per cent. the life is reduced (8).

In electrolytic condensers the purity of the aluminium affects (29)

(*a*) the time of formation of the active layer,
(*b*) the D.C. leakage of the film,
(*c*) the number of cell failures due to corrosion.

As regards the time necessary for formation, this is more rapid with aluminium of 99·6 per cent. purity than of 99·1 per cent. purity. The D.C. leakage is also lower with the purer sample. For example, after formation at 60 V. for 24 hours,

99·1 per cent. pure aluminium passed ca. 3 microamps./cm.^{2}
99·6 per cent. „ „ „ ca. 0·5 „ „

Although purer samples of aluminium appear to be more readily corroded by the electrolyte, the best results in a solution of ammonium borate solution are obtained with a silicon content of 0·24 per cent.

The corrosion that occurs in electrolytic condensers makes itself apparent by pitting of the electrodes, the development of growths at the anode surface, and the deposition of sludge. There is no definite time at which corrosion starts; it may commence soon after a unit has been placed in service, or it may be delayed many months. Even when corrosion has taken place, condenser units will often continue to function for years. This seems to indicate that the corrosive influence may be eliminated after a time by chemical action, and that a protective film then forms over the affected area.

(b) *The Cathode.*

A formed aluminium electrode when made a cathode offers only a small resistance to current flow if the voltage is above a certain minimum value (the Mindestspannung of Schulze). This minimum potential is dependent upon the valve metal, the thickness of the active layer, as well as the nature and concentration of the electrolyte. It is independent of temperature.

In a condenser operating on a D.C. circuit the negative plate serves only to make contact with the electrolyte. Although not subjected to any intentional formation, there is a tendency for a film to form on the cathode (if it is a valve metal) during the periods that the condenser discharges. This may be overcome by using either an inert (non-valve) metal or an aluminium alloy containing sufficient amount of some substance, *e.g.* silicon, which hinders film formation. With an alloy containing less than 99 per cent. aluminium it is possible to have a C.D. of ca. 1 m.a. A.C./cm.^{2} of negative plate without sufficient film forming to affect the capacity of the cell (29).

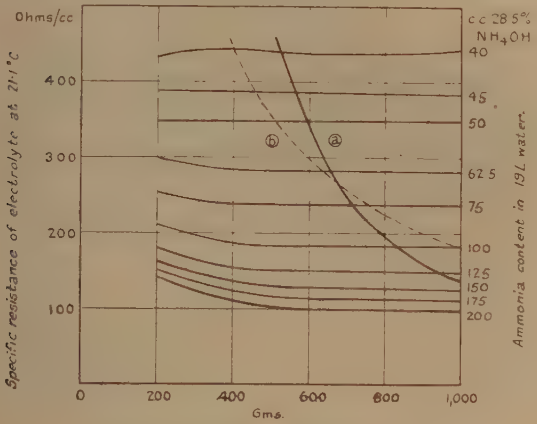
The Electrolyte.

The formation of the anode film takes place in acid or in alkaline solutions. The presence of acid ions in the electrolyte favours the formation of the insulating layer on an aluminium anode; alkaline ions favour its removal when the electrode is made cathode (21). The results obtained with different electrolytes are essentially the same, so long as a similar reaction occurs in each case at the electrode surface, although the electrical characteristics of the cell, such as its resistance and power factor, may be considerably modified. Generally speaking, the electrolytes that have shown themselves to be most suitable are solutions of ammonium or alkali salts of the weak acids such as borates, oxalates, tartrates, citrates, and salts of other organic acids. To assist the formation of aluminium plates C. Pollak (19, 20) adds about 3 per cent. of chromate to an alkaline or neutral electrolyte. Ammonium molybdate has been suggested (1) as a suitable electrolyte. However, one that is suitable for use in a condenser may be quite unsuitable for use in a rectifier.

An electrolyte that has shown itself to be particularly suitable for use in electrolytic condensers as used in telephone work is ammonium borate. The specific resistance of the solution for various proportions of boric acid and ammonia is shown in fig. 5 (29), which exhibits several interesting points. The intersection of the constant ratio boric acid-ammonia curve and the *p*H curve shows that the acidity of the ammonium borate solution decreases with the dilution: by adding sufficient water the solution may be made alkaline. The fact also emerges that the specific resistance of the electrolyte is determined mainly by the ammonia content, and the acidity or alkalinity by the boric acid content, Control of the pH value of borate solutions can also be effected by adding glycerol (39) or certain sugars.

Fig. 5.

Specific resistance of ammonium borate solution. (Siegmund (29).)



Boric acid content in 19 L. water.

(*a*) Neutral solution $p\text{H} = 7{\cdot}0$. (Heavy curve.)
(*b*) Constant proportion of boric acid and ammonium. (Dotted curve.)

In choosing an electrolyte for a condenser regard should be had to the following points :—

(*a*) the specific resistance of the electrolyte and its influence on the electrical characteristics of the unit ;

(*b*) the corrosive action of the solution on the metal electrodes ;

(*c*) the life of the solution : that is to say, taking the case of aluminium, the rate at which it becomes saturated with aluminium hydroxide. During use, the small leakage current of the cell is accompanied by a corresponding solution of the metal.

In general, the lower the specific resistance of the solution the more rapidly the hydroxide forms (see Table VII). Although a high specific resistance is advantageous in reducing the rate of hydroxide formation, it increases the electrical impedance of the cell. The precipitation of hydroxide is more rapid at higher temperatures. Furthermore, when a formed anode is allowed to stand idle, deterioration of the film takes place, due to attack by the electrolyte.

Effect of Impurities in the Electrolyte.

The formation of the anode film is highly sensitive to the presence of impurities in the electrolyte. Strong acids, heavy metals, and halogen, nitrate and chlorate ions destroy the unidirectional conductivity of an aluminium cell. The extremely small amounts of foreign substances that will interfere with the functioning of the cell are evident from the following results of Schulze (27). With an aluminium anode in 0·22 N. borax solution, sodium chloride in a concentration of $2{\cdot}5 \times 10^{-4}$ N. produces a noticeable retardation of forming. This amount is equivalent to ca. ½ per mil. of the borax, and is sufficient to produce a turbidity with silver nitrate solution. Any electrolyte giving this reaction should be rejected for the purpose of electrolytic condensers or rectifiers. Bromine and iodine ions act similarly. The action of sodium nitrate is not so great. A concentration of 0·002 N. (≡1 per cent. of the borax) retards the film formation. A slight alkalinity of the electrolyte is not objectionable, but a strong alkalinity destroys the valve action. Sodium hydroxide in a borax solution will react thus

Table VI.

Sp. resistance of ammonium borate solution.	Approx. life at 25° C. before aluminium hydroxide separates out.
75 ohms.	½–1 year.
150	1–3 years.
300	over 5 years.

$$2NaOH + Na_2B_4O_7 \rightarrow 2Na_2B_2O_4 + H_2O.$$

Seeing that the metaborate is not hydrolysed much more than the tetraborate, the sodium hydroxide will not become effective till its concentration is in excess of that of the borax.

The enormous increase in the leakage current of an aluminium anode when halogen ions are present is shown in

Table VII.(1). The addition to a borax solution of a substance, *e.g.* a sulphate, acetate, etc., which itself will allow film formation, but not to the same extent as borax, will have an unfavourable influence. Taylor and Inglis(34) have found that those salts (*e.g.*, KCl, KNO_3, etc.) that destroy the functioning of an aluminium cell are those that easily diffuse through an aluminium membrane. Other salts that do not diffuse through are without effect.

Condenser Properties of Formed Electrodes.

In considering the electrical properties of the electrolytic condenser, it is impossible not to make considerable reference to the exhaustive work of C. I. Zimmerman (37 & 53).

TABLE VII.

Electrolyte.	Gm. PO_4 ion. *a.*	Gm. Cl ion. *b.*	Ratio $\frac{a}{b} = \sigma$.	$\frac{mA.}{cm.^2}$.	Ratio $\frac{i_\sigma}{i_0}$.
130 c.c. NH_4NaHPO_4.........	0·59	—	—	0·0013	1
130 c.c. NH_4NaHPO_4 +3½ c.c. KCl aq.	0·57	0·048	0·084	0·157	121
+4½ „	0·57	0·062	0·109	0·26	204
+5½ „	0·56	0·076	0·136	0·471	362
+6½ „	0·56	0·090	0·161	0·972	750
+7½ „	0·56	0·105	0·191	1·89	1450

Aluminium anode formed at 110 V. D.C. Measurements made at 20 V. D.C.

The active layer on a formed aluminium electrode constitutes an asymmetric dielectric, in that it can retain positive charges only on the side in contact with the metal. A single formed electrode immersed in electrolyte constitutes what is termed an asymmetric cell. Compared with an ordinary mica or plate condenser, the metal anode and the electrolyte correspond to the two conducting coatings, and the active layer or film to the dielectric. Two formed electrodes immersed in an electrolyte (two series-opposed asymmetric cells) are equivalent to two ordinary plate condensers in series, but the distribution of electrostatic charges internally is quite different from that which obtains in two series connected plate condensers, on account of the rectifying properties of the film. The potentials across the two films of an electrolytic condenser are in opposition to each other, whereas in the case of two series connected plate condensers the potentials across the individual dielectrics act in series. The condenser action of two series-opposed asymmetric cells results from the energy changes accompanying the variations in distribution of the constant charge held by the unit. Such an arrangement will not allow D.C. to pass; A.C. will, however, pass, producing a leading current in the circuit in which it is incorporated.

On connecting an electrolytic condenser consisting of two series-opposed asymmetric cells to an A.C. source of voltage, current flows until the impressed voltage on the cell terminals has reached its maximum. One electrode of the cell now has maximum voltage applied to it, and therefore has its maximum charge. As the potential decreases from its maximum value, the electrode which was positive starts to discharge into the circuit, and the charge which it held accumulates on the other electrode making this one now positive. For any subsequent variation of voltage the total coulomb charge remains constant (for a given maximum applied voltage), whereas in an ordinary plate condenser the charge varies with the applied voltage. The constant electrostatic charge existing in the cell sets up a uniform difference of potential between the electrolyte and any point outside the cell in the external circuit which is neutral with respect to the A.C. pressure. The electrolyte is always negative with respect to the neutral A.C. pressure reference point. The arithmetical sum of the potentials across the two films is constant, and equals the maximum voltage impressed on the condenser terminals. The algebraic sum of the instantaneous values equals the instantaneous value of the impressed voltage. The potential difference existing between the electrolyte and either electrode is the resultant of a uniform potential equal to one-half the maximum instantaneous value of the voltage impressed on the cell, and an A.C. voltage equal to one half the effective value of the voltage impressed on the cell. This is a pulsating unidirectional pressure. Each film is subjected to an A.C. component equal to one half the pressure impressed on the condenser; and each film is subjected to the maximum pressure impressed on the cell, instead of one-half as is the case with two ordinary plate condensers connected in series.

Energy Variation within the Cell.

It has been mentioned above that when the charge on one electrode is at a maximum, the charge on the other is zero.

The energy stored at the maximum voltage is therefore

$$W_1 = \tfrac{1}{2} QE_{\text{max.}}$$

where Q $\quad$ = the charge in coulombs,

$E_{\text{max.}}$ = the maximum voltage.

At the moment the applied voltage becomes zero, each film holds one half the charge at one half the voltage; the stored energy then amounts to

$$W_2 = 2\left[\frac{1}{2} \times \frac{1}{2} \times \frac{E_{\text{max.}}}{2}\right]$$

$$= \tfrac{1}{4} QE_{\text{max.}}$$

The energy variation is therefore $W_1 - W_2 = \tfrac{1}{4} QE_{\text{max.}}$, or one half the total energy stored in the condenser when maximum voltage is impressed on the terminals. Whereas an electrolytic condenser (two series-opposed asymmetric cells) stores and gives up only one half of its total charge, an ordinary condenser stores and gives up its total charge. In the electrolytic condenser one film charges while the other discharges; in an ordinary condenser both electrodes charge and discharge together.

When the two electrodes in an electroytic condenser are not of the same electrostatic capacity, the charge stored in the condenser is independent of the capacity of the smaller electrode, and is determined solely by the maximum charge capable of being stored by the larger electrode. If one of the electrodes of the cell has negligible capacity, the unit no longer reacts on an A.C. circuit like an ordinary condenser, since it is able to receive a charge but unable to return it. In such a cell the potential difference between the smaller electrode and the electrolyte has a theoretical maximum value of twice the maximum pressure applied to the cell terminals.

Considerations of the electrical properties of polyphase electrolytic condensers have also been made by Zimmermann (38).

Electrical Losses of the Electrolytic Condenser.

The losses associated with the electrolytic condenser are made up as follows :—

(*a*) A loss constant at all frequencies due to the inherent conductivity of the film, and which is equivalent to a high resistance in parallel with the capacity.

(*b*) Dielectric loss which, as in the case of the ordinary type of condenser, increases with frequency.

(*c*) I^2R losses due to the resistance of the electrolyte. Since the most suitable electrolytes for electrolytic condensers have a low conductivity, the losses due to this cause may be appreciable. The resistance of the electrolyte remains almost constant over a very wide range of frequencies.

(*d*) Losses due to electrolytic decomposition.

The composition of the electrolyte has considerable influence on the power factor of an electrolytic condenser when used on an A.C. circuit. For example, an electrolyte of the composition

30 gm. boric acid,
5 „ ammonium borate,
1 L. water,

Table VIII.

Condenser.			Calculated capacity. mF.	Power factor.	Temp. °C.	Formation voltage. D.C.	Residual current at D.C. forming voltage. Amp.	Peak value of applied A.C.	Time of closed A.C. circuit. Mins.
Current. Amps.	Voltage. A.C.	Losses. Watts.							
1·26	27·4	2·25	146·3	0·065	19·7	40	0·003	ca. 33	120
1·35	59·2	4·0	72·6	0·050	18·0	80	0·0045	„ 84	60
1·72	113·4	23·0	48·2	0·118	22·8	160	0·0037	„ 159	60

exhibits a P.F. of 40 per cent.; whilst the same solution with 4 gm. sodium hydroxide and ½ gm. sodium fluoride added exhibits a P.F. of 4·2 per cent. (13).

In Table VIII. are given some results obtained by Schulze (25) on an aluminium condenser working on A.C. The condenser consisted of ten plates of aluminium 9·7 × 16·5 × 0·1 cm. immersed in saturated ammonium borate ($(NH_4)HB_2O_4$); alternate plates were aranged to be anode and cathode. The P.F. increases as the value of the applied A.C. voltage increases (see Table IX.), and also with the time of closed circuit.

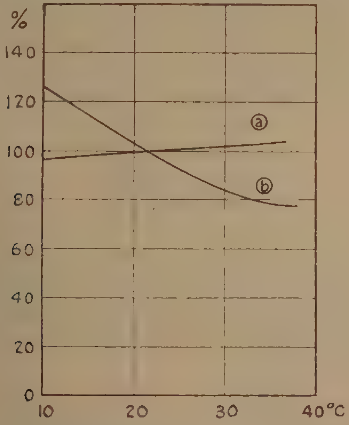
The condensers described by Siegmund (29), utilizing a solution of ammonium borate of specific resistance 225 ohms, have P.F.'s of the order of 9 per cent. measured at 60 cycles. In Table X. are given some values at different frequencies of the capacity and equivalent series resistance for this type of condenser ; fig. 6 shows the percentage variation in these values with temperature.

TABLE IX.

Calculated capacity. mF.	Voltage. A.C.	Current. Amp.	Losses. Watts.	Power factor.
43·9	102·8	1·42	8·6	0·059
43·9	82·8	1·14	5·0	0·053
43·8	73·6	1·01	3·5	0·047
43·6	59·2	0·81	1·7	0·041

Fig. 6.

Percentage variation ϕ, with temperature, of capacity and equivalent series resistance of 48 V. condenser at 1000 ∼. (Siegmund (28).)



(*a*) Capacity curve.
(*b*) Equivalent series resistance curve.

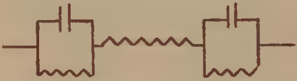
Various equivalent networks have been suggested as corresponding to a valve anode. N. A. de Bruyne and R. W. W. Sanderson ((2) *q.v.* for other references) assumed for experimental purposes that an electrolytic condenser

TABLE X.

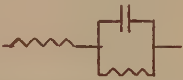
	Frequency.	Initial value.	Value after one year's service.
Capacity.	60 ~	640 mF.	930 mF.
	400	570	860
	1000	540	840
	2000	520	830
Equivalent series resistance.	60 ~	0·37 ω	0·27 ω
	400	0·15	0·125
	1000	0·14	0·12
	2000	0·12	0·11

Condenser formed at 100 V. D.C. and operated continuously for one year at 66 V. D.C. (Values have been read from a small scale graph.)

having two similar plates was equivalent to the following network :—



The capacities shunted by the resistances represent the leaky condensers at the electrodes, and the series resistance the resistance of the electrolyte. For two electrodes of equal area this network reduces to



In such a simple network, which lends itself to calculation, the values of the component parts were shown to be not independent of frequency. It would appear that there is no simple network which is capable of accurately representing the electrolytic condenser.

Applications of the Valve Anode.

The unidirectional current conducting characteristic of aluminium and tantalum anodes has found wide use for the rectification of A.C. to supply a source of D.C. for battery charging. The best results for rectification are obtained with high current density at the anode ; low inductance and resistance of the external circuit ; and low temperature. The capacity effect in the action of the valve lowers the

E.M.F. of the the rectified current (17). In consequence of the low conductivity of the electrolyte and the high resistance of the film, the I^2R losses are high. The use of a high current density for rectification purposes means that the I^2R heat is limited to a small space, and therefore there results a considerable rise in temperature, which must be kept down by using a large volume of electrolyte or by fitting special means for cooling the electrodes or electrolyte. As cathode in electrolytic rectifiers it is usual to use lead, iron, or carbon electrodes, and often the metal container itself.

The high resistance of the aluminium film to the passage of electric current has been utilized for preventing arcs on interrupting an inductive circuit (10). The B.D.V. of the electrolytic cell for this purpose should be greater than the normal working voltage of the circuit. On interrupting an inductive circuit the high voltage surge breaks down the film, which reforms when the circuit is operated again. The break-down characteristic of the aluminium anode is utilized in addition for the production of electrolytic lightning arrestors.

The high electrostatic capacity available at a valve anode has been utilized for the production of static condensers. The high losses associated with electrolytic condensers on A.C. circuits, however, precludes their use at high frequency voltages. Their usefulness is restricted to employment on low voltage circuits for protection against surges of steep wave front, and for use on D.C. circuits where it is desired to filter out an A.C. ripple.

In telephone work it has been the practice to build special generators which will give a smooth D.C. output that will not interfere with conversations when connected to telephone circuits. The ordinary commercial generators can be employed for charging the exchange battery associated with the telephone circuits, when used in conjunction with a filter circuit comprising chokes and condensers, which eliminates the ripple present in the current supplied by the power plant, and thereby cuts out hum from the telephone circuits (36).

When an electrolytic condenser is used on a D.C. circuit it is sufficient to have a cell with one electrode of a valve metal such as aluminium, and one electrode of a non-valve metal. The condenser action is assured so long as the valve metal is kept positive. Such an arrangement on an A.C. circuit will act rather as a rectifier

Aluminium condensers have been used for the production of high voltage D.C. (31). Several cells are connected in series and charged rapidly one after another by a rotating commutator; the whole set of cells is discharged in series.

The bulk and cost per microfarad of an electrolytic condenser are considerably less than that of an ordinary condenser operating at the same voltage. However, at higher voltages, where the efficiency is not so great, this economy is not so apparent, since the energy storing capacity of a condenser varies as the square of the impressed voltage.

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III. *A Note on Doppler Effect and the Hypothesis of Radiation Quanta.* By D. S. KOTHARI, *M.Sc., Demonstrator in Physics, Allahabad University* *.

THE Doppler-Fizeau effect, which has been so widely applied in several astrophysical problems, is easily explained if radiation is considered to be propagated in the form of waves. In the present note it is explained on the hypothesis of radiation quanta, *i. e.*, light is considered to be propagated in the form of quanta and not waves. It is further shown that Compton effect is a particular case of Doppler effect.

§ 1.

Let us consider a source S which emits waves of wave-length λ and frequency ν, moving with velocity u towards a stationary observer O.

Owing to the motion of the source the waves will be compressed a little, and the wave-length λ_s will be †

$$\frac{\lambda_s}{\lambda}=\frac{c-u}{c}$$

or

$$\Delta\lambda_s=-\frac{u}{c}\lambda\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for $\frac{u}{c}$ is small in all practical cases.

If the observer is moving with velocity u towards the stationary source, it is easily seen that

$$\frac{\lambda_0}{\lambda}=\frac{c}{c+u},$$

$$\Delta\lambda_0=-\frac{u}{c}\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In the case of rays reflected at an angle z from a mirror moving forward along the direction of its normal with velocity u,

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* Communicated by Prof. M. N. Saha, F.R.S.

† R. A. Houstoun, 'A Treatise on Light,' p. 275.

$$\frac{\lambda_m}{\lambda}=\frac{1-\frac{u}{c}\cos z}{1+\frac{u}{c}\cos z},$$

where λ_m is the wave-length of the reflected light,

$$\therefore \qquad \Delta\lambda_m=\frac{2u\cos z}{c}.$$

According to the relativity hypothesis the velocity of light in free space is always equal to c. The Doppler effect is, however, easily accounted for, provided light is regarded as wave-motion.

Let the waves*

$$\psi=\mathrm{A}\cos\frac{2\pi}{\lambda}(lx+my+nz-ct)$$

appear to the observer moving with velocity u towards the source as

$$\psi'=\mathrm{A}'\cos\frac{2\pi}{\lambda'}(l'x'+m'y'+n'z'-ct').$$

As the second expression when subjected to Lorentz transformation should reduce to the first, we have

$$\frac{\lambda'}{\lambda}=k\left(\frac{c-l'u}{c}\right), \qquad k=\frac{1}{\sqrt{1-\frac{u^2}{c^2}}},$$

$$\frac{\lambda'}{\lambda}=1-\frac{u}{c}\cos\theta, \text{ for } l'=\cos\theta$$

$$\text{or} \qquad \Delta\lambda=-\frac{u}{c}\cos\theta\,.\,\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

θ being the angle which the ray appears to make with the X-axis or the direction of u.

This result is the same as was obtained formerly on the classical theory. If the radiation be regarded in the form of waves, the Doppler effect is easily accounted for on the classical, and is not inconsistent with the relativity, theory.

In a previous note† the shift in wave-length on reflexion at a moving mirror has been deduced on the hypothesis of radiation quanta. In that derivation the conception of radiation pressure is made use of (*i. e.*, the process is considered from a statistical point of view), and the exact mechanism as to how the change in wave-length is brought about is not considered.

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* *Ann. der Phys.* xvii. p. 910 (1905).

† B. N. Srivastava and D. S. Kothari, "A Note on Wien's Displacement Law etc.," sent to the Indian Journ. Phys.

The results here derived are mainly in a way an application of the fundamental ideas advanced by Prof. Saha regarding selective radiation pressure.

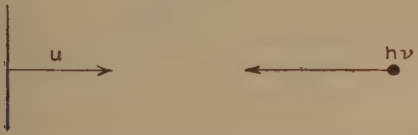
§ 2.

Doppler effect in the case of normal incidence on a mirror moving along its normal.

M = mass of the mirror.

Let a quantum $h\nu$ be incident, and after reflexion its frequency be ν_m. Let u be the velocity of the mirror before the incidence of the quantum, and v its velocity just after reflexion. The velocity of the quantum will always be c, as required by the theory of relativity and the experiments of Q. Marjorana *.

Fig. 1.



We have the energy equation,

$$\tfrac{1}{2}\mathrm{M}u^2+h\nu=\tfrac{1}{2}\mathrm{M}v^2+h\nu_m, \quad . \quad . \quad . \quad . \quad (5)$$

and the momentum equation,

$$\mathrm{M}u-\mathrm{M}v=\frac{h\nu}{c}+\frac{h\nu_m}{c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Eliminating v, we obtain :

$$\frac{1}{2}\frac{h^2}{mc^2}(\nu+\nu_m)^2-\frac{hu}{c}(\nu+\nu_m)+h(\nu_m-\nu)=0,$$

$$\Delta\nu=\nu_m-\nu=\frac{2u}{c}\nu-\frac{2h\nu^2}{mc^2};$$

$$\therefore \quad \Delta\lambda_m=\lambda_m-\lambda=-\frac{2u}{c}\lambda+\frac{2h}{mc}. \quad . \quad . \quad . \quad . \quad (7)$$

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* Phil. Mag. xxxv. and xxxvii.

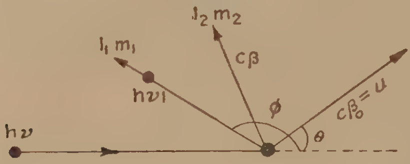
Now, $\frac{h}{mc}$ will be negligible, unless m be very small,

$$\Delta\lambda_m = -\frac{2u}{c}\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

a result identical with (4) for the value $\theta=0$, *i. e.*, normal incidence, as is here considered.

Let us now consider a more general case, *i. e.*, of a body of mass M moving initially with velocity $c\beta_0$ along the direction making an angle θ with the direction of the incident quantum $h\nu$.

Fig. 2.



$l_1 = \cos\phi$ }
$m_1 = \sin\phi$ } direction cosines of the reflected quantum $h\nu'$.

l_2, m_2 ...... direction cosines of the velocity of M after the reflexion of the quantum :

$$h\nu + mc^2\left(\frac{1}{\sqrt{1-\beta_0^2}}-1\right) = h\nu' + mc^2\left(\frac{1}{\sqrt{1-\beta^2}}-1\right), \quad \text{(i.)}$$

$$\frac{h\nu}{c} + \frac{m\beta_0 c}{\sqrt{1-\beta_0^2}}\cos\theta = \frac{h\nu'}{c}l_1 + \frac{m\beta c}{\sqrt{1-\beta^2}}l_2, \quad . \quad . \quad \text{(ii.)}$$

$$\frac{m\beta_0 c}{\sqrt{1-\beta_0^2}}\sin\theta = \frac{h\nu'}{c}m_1 + \frac{m\beta c}{\sqrt{1-\beta^2}}m_2. \quad . \quad \text{(iii.)}$$

Putting
$$\alpha = \frac{h\nu}{mc^2},$$

$$\alpha' = \frac{h\nu'}{mc^2},$$

$$b_0 = \frac{\beta_0}{\sqrt{1-\beta_0^2}}, \qquad b = \frac{\beta}{\sqrt{1-\beta_0^2}},$$

we have

$$\frac{1}{\sqrt{1-\beta_0^2}} = \sqrt{1+b_0^2},$$

$$\frac{1}{\sqrt{1-\beta^2}} = \sqrt{1+b^2},$$

$$\alpha = \alpha' + \sqrt{1+b^2} - \sqrt{1+b_0^2}, \quad . \quad . \quad . \quad \text{(iv.)}$$

$$\alpha + b_0 \cos\theta = \alpha' l_1 + b l_2, \quad . \quad . \quad . \quad . \quad \text{(v.)}$$

$$b_0 \sin\theta = \alpha' m_1 + b m_2. \quad . \quad . \quad . \quad . \quad \text{(vi.)}$$

From (v.):

$$b^2 l_2^2 = \alpha^2 + \alpha'^2 l_1^2 - 2\alpha\alpha' l_1 + b^2 \cos^2\theta + 2b_0 \cos\theta(\alpha - \alpha' l_1).$$

From (vi.):

$$b^2 m_2^2 = b_0^2 \sin^2\theta + \alpha'^2 m_1^2 - 2\alpha' m_1 b_0 \sin\theta\,;$$

$$\therefore \quad b^2 = \alpha^2 + \alpha'^2 + b_0^2 - 2\alpha\alpha' l_1 + 2b_0 \cos\theta(\alpha - \alpha' l_1) - 2\alpha' m_1 b_0 \sin\theta. \quad \text{(vii.)}$$

From (iv.):

$$b^2 = \alpha^2 + \alpha'^2 + b_0^2 - 2\alpha\alpha' + 2\sqrt{1+b_0^2}(\alpha - \alpha').\,. \quad \text{(viii.)}$$

From (vii.) and (viii.)*:

$$\frac{\alpha}{\alpha'} = \frac{\lambda'}{\lambda} = \frac{\alpha(1-l_1) + \sqrt{1+b_0^2} - b_0(l_1\cos\theta + m_1 \sin\theta)}{\sqrt{1+b_0^2} - b_0\cos\theta}\,;$$

$$\therefore \quad \Delta\lambda_m = \frac{\lambda(1-l_1)(\alpha + b_0\cos\theta) - b_0 m_1 \sin\theta}{\sqrt{1+b_0^2} - b_0\cos\theta}.$$

$$\alpha = \frac{h\nu}{mc^2} = \frac{h}{mc\lambda},$$

$$b_0 = \frac{\beta_0}{\sqrt{1-\beta_0^2}} = \beta_0, \text{ when } \beta_0 << 1\,;$$

$$\therefore \quad \Delta\lambda_m = \frac{2u}{c}\lambda \sin\frac{\phi}{2} \sin\left(\frac{\phi}{2} - \theta\right) + \frac{h}{mc} \operatorname{vers}\phi. \quad . \quad . \quad (9)$$

In the case of a mirror moving forward with velocity u along its normal,

$$\theta = \pi - z, \qquad \phi = \pi - 2z\,;$$

$$\therefore \quad \Delta\lambda_m = -\frac{2u}{c}\cos z + \frac{h}{\mathrm{M}c} \operatorname{vers}\phi,$$

$$= -\frac{2u}{c}\cos z \text{ when M is not very small.}$$

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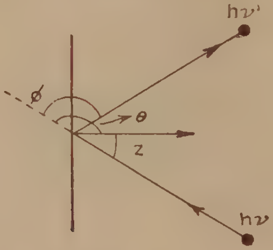
* This result has been arrived at from "Relativity Theory," by Dirac, M. N., R. A. S. 1925.

This is a result exactly identical with relation (3) above.

Fig. 3.



In the equation (9) above, if $u=0$, *i. e.*, the reflector be at rest, there is still a change in wave-length,

$$\Delta\lambda = \frac{h}{\mathrm{M}c}(1-\cos\phi).$$

This is the well-known expression for Compton effect*. When the shift in wave-length is considered on the hypothesis of radiation quanta, it becomes evident that Compton effect is nothing but Doppler effect observed with a body at rest. Similarly, we might say that Doppler effect is but Compton effect observed with a body in motion.

§ 3.

(i.) *Doppler effect due to the motion of the source*:—Let us consider the source of mass m moving with velocity u towards the observer. We can easily put down the energy and the momentum equation :

$$\tfrac{1}{2}mu^2 + h\nu = \tfrac{1}{2}mv^2 + h\nu',$$

$$mu = mv + \frac{h\nu'}{c};$$

$$\therefore \quad h\nu - h\nu' = \frac{1}{2}\frac{h^2}{mc^2}\nu_1{}^2 - \frac{h}{c}u\nu_1;$$

$$\therefore \quad \frac{\nu}{\nu'} = \frac{\lambda'}{\lambda} = \frac{c-u}{c} + \frac{1}{2}\frac{h}{mc\lambda}$$

$$\text{or} \qquad \left.\begin{aligned} \frac{\lambda'}{\lambda} &= \frac{c-u}{c}, \\ \Delta\lambda &= -\frac{u}{c}\lambda; \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

results identical with those given in § 1, equation (1).

* Phys. Rev. xx. (1923).

(ii.) *Doppler effect due to the motion of the observer* :—When radiation is regarded in the form of quanta, at first sight it is not possible to see how a motion of the observer can bring about a change in wave-length. However, on the above lines the shift in wave-length is readily deduced.

Let the observer move with velocity u towards the source. The energy and the momentum equations in this case will be :

$$h\nu + \tfrac{1}{2}mu^2 = h\nu' + \tfrac{1}{2}mv^2,$$

$$mu - \frac{h\nu}{c} = mv,$$

$m =$ mass of the observer;

$$\therefore \quad \nu - \nu' = \frac{1}{2}\frac{h\nu^2}{mc^2} - \frac{u}{c}\nu;$$

$$\therefore \quad \frac{\nu}{\nu'} = \frac{\lambda'}{\lambda} = \frac{c}{c+u} + \frac{1}{2}\frac{h}{mc\lambda}$$

$$\text{or} \quad \left.\begin{aligned} \frac{\lambda'}{\lambda} &= \frac{c}{c+u}, \\ \Delta\lambda &= -\frac{u}{c}\lambda; \end{aligned}\right\} \quad \ldots\ldots \quad (12)$$

results identical with those of § 1, equation (2).

The Doppler effect for a source at rest is not zero, but

$$\Delta\lambda_s = \frac{1}{2}\frac{h}{mc}.$$

This shows that if an atom at rest in an excited state W_n returns to the lower state W_m, the frequency of the quantum emitted is not $\dfrac{W_n - W_m}{h}$ but

$$\frac{W_n - W_m}{h} - \frac{1}{2}\frac{(W_n - W_m)^2}{mc^2h}.$$

The wave-length is not that corresponding to $W_n - W_m$, but is increased by $\dfrac{1}{2}\dfrac{h}{mc}$. This increase in wave-length is, however, very small, in the case of even an H atom it being only 6×10^{-6} Å.U. This may be termed the Compton effect for emission.

Similarly, an atom at rest when undergoing a transition from the m state to the n state does not absorb a quantum of frequency $\dfrac{W_n - W_m}{h}$, but one having the frequency,

$$\frac{W_n - W_m}{h} + \frac{1}{2}\frac{(W_n - W_m)^2}{mc^2 h}.$$

This shows that the wave-length of the quanta emitted and absorbed by the same atom are not absolutely equal, but differ by $\frac{h}{mc}$.

Note I. Doppler effect for a rotating source :—Let us consider the Doppler shift for a quantum emitted tangentially at a distance r from the axis of rotation. Let ω_1 be the velocity of rotation before emission, and ω_2 just after emission ; we have

$$\tfrac{1}{2}I\omega_1^2 + h\nu = \tfrac{1}{2}I\omega_2^2 + h\nu',$$

and the conservation of angular momentum gives

$$I\omega_1 = I\omega_2 + \frac{h\nu'}{c} r$$

(I = moment of inertia of the body about the axis of rotation) ;

$$\therefore \quad \Delta\lambda = -\frac{\omega_1 r}{c} . \lambda,$$

i. e., the same shift that corresponds to the translational velocity $\omega_1 r$ along the line of emission at the point from where the quantum is emitted.

Note II. The second postulate of relativity, *i. e.*, the constancy of the velocity of light, has been subjected to an experimental test by Q. Majorana[*]. The experiment consists in measuring the wave-length change due to Doppler effect by using the Michelson interferometer. It is shown that different results should be obtained for the shift according as the hypothesis for the constancy of c is admitted or not, *i. e.*, if it be constant,

$$\Delta\lambda = -\frac{u}{c}\lambda ;$$

whereas if the velocity of light emitted from a source moving with velocity u be not c but $c+u$,

$$\Delta\lambda = 0.$$

In arriving at these results the radiation is regarded in the form of waves. Hence, strictly speaking, the Majorana experiment, as interpreted in the original paper, demonstrates the constancy of the velocity of light, provided light be regarded as wave-motion.

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[*] *Loc. cit.*

As it has been shown that the Doppler effect is explicable on the hypothesis of radiation quanta, the Majorana experiments can therefore be regarded as proving the constancy of c, no matter whether we consider light as propagated in the form of waves or quanta.

My best thanks are due to Prof. M. N. Saha, F.R.S., for his kind interest throughout the work.

IV. *Talbot's Law in Photoelectric Cells.*

By Norman Campbell, *Sc.D.**.

I WOULD offer two observations on the paper by Messrs. Carruthers and Harrison on this subject †.

I. There is a simpler explanation of their results than that which they offer. Their experiments prove that, in certain circumstances in which the time average of the current through the cell is not proportional to the time average of the illumination upon it, the latter average is still determined by the former (Talbot's law). The failure of proportionality in these circumstances they attribute to "fatigue"; and they are doubtless right, though I should prefer to abandon the question-begging word "fatigue" and to say that the emission of the cell (*i.e.*, the ratio of primary photoelectric current to illumination) varies with the period during which the cell has been exposed to illumination. In order to explain why Talbot's law holds, even when there is such variation of the emission, they discuss the changes of the emission that are likely to occur during each cycle of the intermittent illumination.

But, apart from the observations of their last paragraph (which they admit to be not wholly conclusive), there is no evidence of such changes. The whole matter would be explained if there were no appreciable change of emission during a cycle, if the whole of the change took place in the much longer period during which the instrument is taking up its final reading, and if the amount of the change were determined wholly by the time average of the illumination. This last hypothesis is very plausible. For, in some cells at least, most of the change is due to temperature changes, and the temperature will, of course, be determined by the time average of a rapidly fluctuating illumination. In fact, since "fatigue" is almost certainly due to redistribution of films of gas and metal in the cell, any factor producing "fatigue" is likely to be so determined.

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* Communicated by the Author.

† Phil. Mag. vii. p. 792 (1929).

II. That Talbot's law holds when there is "fatigue" is interesting, but not practically important. For since, as Messrs. Carruthers and Harrison point out, there are cells that have no fatigue, the proper way to deal with complications arising from fatigue is not to use cells that have it. But proportionality between illumination and current may fail for another reason, much more important practically. Near the sparking potential of a gas-filled cell, the form of the voltage characteristic and the magnification due to ionization by collision vary with the illumination. When there is failure of proportionality from this cause (which becomes appreciable when considerable illuminations are applied with voltages just below the sparking potential), Talbot's law cannot possibly hold generally; for the voltage can be set so that the cell sparks when a fluctuating illumination is applied of which the time average is the same as that of a steady illumination for which it does not spark.

It is necessary, therefore, to issue a warning to those not familiar with the vagaries of gas-filled cells that it has *not* been proved that Talbot's law is always valid, even when there is failure of proportionality.

V. *Talbot's Law in Photoelectric Cells.*

By T. H. Harrison *and* W. S. Stiles [*].

IN reply to the comments by Dr. Campbell on the paper by Carruthers and Harrison on this subject, we should like to draw attention to the following points.

In our experiments and analysis [†] we are not concerned with the primary photoelectric current (*i.e.*, the rate of liberation of photoelectrons), but with the total current passed by the cell, some of which is due to ionization by collision. By "fatigue" we mean merely the change with time in this current when the cell is exposed to constant illumination. It is agreed that the word "fatigue" is used for want of a more suitable term.

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[*] Communicated by the Authors.

[†] Carruthers and Harrison, Phil. Mag. vii. p. 792 (1929), cited as I.; Stiles, Phil. Mag. vii. p. 812 (1929), cited as II.

With respect to the suggested alternative explanation of our results put forward by Campbell, it is difficult to see in what way his view differs from ours. In both papers I. and II. no theory is advanced as to the causes of "fatigue" effects, which we think may possibly arise in the manner suggested by Campbell. Campbell's view, indeed, requires just such effects as were detected experimentally (final paragraph of paper I.). The change of emission during a light period will admittedly be very small, particularly at high sector speeds, but the rate of change with time will nevertheless still be of significance, and will, we think, determine the steady state which the cell will finally take up under the flickered illumination. The change with which Campbell is concerned is the transitory change taking place immediately after exposure either to flickered or to steady light. The fact that Talbot's law is obeyed after allowing only 5 seconds to elapse seems to indicate that this rapid fatigue must necessarily occur both from our detailed discussion and from Campbell's general considerations. The advantage of dealing with the problem analytically is, we think, made clear by the information deduced as to the variation with light intensity of both the initial current and the final current through the cell for steady illumination.

In the case of a cell used in the unstable condition on the point of arcing, it is certain that Talbot's law will not be obeyed for low sector speeds, but for high sector speeds which do not allow sufficient time for the arc-discharge to develop it is feasible that the law will hold good, although we have no direct evidence at the moment. Since, however, for photometric measurements it is inadvisable to use a cell near the arcing-point, this question is not of practical importance.

It is as well to point out that in the gas-filled cells used there was certainly some ionization due to collisions, and yet at the lowest sector speeds worked with (six alternations per second) Talbot's law was obeyed. It is inevitable that, for a non-proportional cell, the law must break down for sufficiently low sector speeds, although this effect could not be obtained experimentally owing to the failure of the measuring system to integrate satisfactorily at such low speeds.

VI. *On the Vibration of Beams under the Action of Moving Loads.* *By* H. H. Jeffcott, *Sc.D.*[*]

Introductory.

1. THE object of this paper is to present an account of a method for the approximate solution of the problem of the vibrations of beams under the action of moving and fluctuating loads.

Considerable attention has recently been given to this problem on account of its fundamental importance in connexion with railway bridges. The methods so far employed for its solution, however, do not appear to be perfectly general in their applicability, and the problem of the vibrations of a heavy bridge under the influence of a moving mass is not directly soluble by them.

The method to be described here is one of successive approximation and is applicable to all cases in which the damping forces and the effective forces due to the acceleration of the masses involved exercise a relatively small influence on the deflexion of the beam in comparison with that produced by the applied forces.

2. It is hardly necessary to make a plea for the adoption of approximate methods for the solution of problems in the theory of beams.

The ordinary Bernoulli Eulerian theory of beams is itself based on physical conceptions of an approximate character. Thus the beam is supposed to be very long compared with its cross-sectional dimensions; the elastic conditions are assumed to be satisfied to the very ends of the beam; plane sections normal to the axis are assumed to remain plane after bending; the principal axes of the section are supposed to be vertical and horizontal; Hooke's law is assumed to hold good for the separate fibres; the material is supposed to be uniform and isotropic or æolotropic throughout; and the theory requires that the deflexions shall everywhere be very small. Furthermore, in the application of the theory assumptions are made in regard to the way in which the ends of the beam are supported, and these are ordinarily chosen to be either free or built in, but in practice such ideal terminal conditions may not be exactly realized.

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[*] Communicated by the Author.

It may also be difficult to express the loads with precision.

Accordingly, the usual theory applied to beams and the hypotheses on which any particular calculation is based are of an approximate kind. Moreover, the conditions of maintenance of the structure and the necessity of applying to the results of calculation a large factor of safety, indicate conclusively that an approximate solution of the problem of the vibrations of beams is not only entirely justified but also sufficient for practical requirements.

3. Approximate methods for the solution of the equations involved may be introduced, broadly, in two ways. Firstly, the mathematical equations may be solved rigorously and approximations may then be introduced into the solutions in their application to engineering problems. Or secondly, approximations may be introduced into the equations before solution or into the mathematical processes of solution. The latter course will often simplify the procedure and facilitate the obtaining of an approximate solution more than the former method, and although it may be less rigorous mathematically, the final result may nevertheless be quite sufficiently accurate.

The conditions of the problem under consideration justify the use of a method falling into the latter category. It is to be observed that the deflexions of the beam are always small quantities compared with its length, and having regard to the magnitude of the velocities contemplated in the problem, the length of span, etc., it appears that in a forced vibration the effective forces due to the acceleration of the particles of the beam and of the moving load, as well as those due to damping, are small in their influence on the deflexion of the beam compared with the applied forces of the problem.

In these circumstances the method of successive approximation to be described is applicable for finding a particular integral.

This method has previously been * used by the author for the solution of the equations of motion of water surging in a pipe connected with a surge chamber, in which the friction of the water on the walls of the pipe exerts a small, though appreciable, influence on the motion.

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* H. H. Jeffcott, Sci. Proc. Roy. Dublin Soc. vol. xviii. (n. s.) no. 6, pp. 63–66 (1924).

The equation of vibration.

4. The equation expressing the motion of vibration of a heavy beam under the action of moving forces is usually of the type

$$\frac{d^4y}{dx^4}+a\frac{d^2y}{dt^2}+b\frac{dy}{dt}=f(x,t),$$

where y represents the deflexion at the point x, a depends on the mass per unit length of the beam, b depends on the damping, and $f(xt)$ is a function of the position x and of the time t.

The complete solution of this equation consists of two parts :—(1) a particular integral of the equation, the simpler the better, and (2) the complementary function, or solution of the equation with the right-hand side replaced by zero. The particular integral represents the forced vibration, while the complementary function represents the free vibration. The complete solution must satisfy the given end conditions and must also yield the initial state of the beam when $t=0$. These considerations serve to determine the constants of integration in any particular case.

5. In the problem of vibrations of beams the principal analytical difficulty arises in finding a particular integral of the differential equation.

Stokes[*] used the method of definite integrals for the solution of the case of a heavy mass moving along a massless beam. The method of harmonic analysis has been employed by Timoshenko[†], Inglis[‡], and Howland[§], in finding the vibrations of a heavy beam subjected to a moving or pulsating force. The general problem of the vibration of a heavy beam under the influence of a moving mass appears to fall outside the possibilities of these methods of attack.

The method of approximate solution.

6. The method here proposed for finding a particular integral of the differential equation is one of successive approximation, and leads to a solution of algebraic type which may often be more convenient than a harmonic series.

It is based on the assumption that in all problems to which it may be applied the effect of the forces $a\dfrac{d^2y}{dt^2}$ and $b\dfrac{dy}{dt}$ on the deflexion at every point is always small compared with that of the applied load $f(xt)$.

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[*] Sir G. G. Stokes, Trans. Camb. Phil. Soc. vol. viii. p. 707 (1849).

[†] Prof. S. P. Timoshenko, Phil. Mag. vol. xliii. p 1018 (1922).

[‡] Prof. C. E. Inglis, Min. Proc. Inst. C. E. vol. ccxviii. p. 225 (1924).

[§] R. C. J. Howland, "Transverse Oscillations in Girders," Inst. C. E. Selected Engineering Papers, no. 23 (1924).

The method consists firstly in omitting the relatively unimportant terms $a\dfrac{d^2y}{dt^2}$ and $b\dfrac{dy}{dt}$ and solving the equation. This gives a first approximation to the value of y in terms of x and t.

The next step is to substitute in the original equation this value of y in the terms $a\dfrac{d^2y}{dt^2}$ and $b\dfrac{dy}{dt}$ and solve the resulting equation. The value of y thus obtained is a second approximation to the solution.

Again, by substituting this more approximate value of y in the terms $a\dfrac{d^2y}{dt^2}$ and $b\dfrac{dy}{dt}$, a third approximation can be found in like manner; and so on.

If the true value of y were known and were substituted in the terms $a\dfrac{d^2y}{dt^2}$ and $b\dfrac{dy}{dt}$, the resulting equation would give as its solution the true value of y. In the absence of such knowledge we gradually approach the true value by successive steps.

The degree of approximation of the value resulting from the omission of the acceleration and damping terms depends on the relative importance of their influence on the deflexion compared with the applied load.

When the resulting approximate value of y is substituted in the terms $a\dfrac{d^2y}{dt^2}$ and $b\dfrac{dy}{dt}$, their significance is expressed more accurately than when they were omitted and the resulting value of y is a better approximation; and so on. A second approximation will usually be sufficient in the problems here considered.

The examples that follow will serve to illustrate the principles involved.

7. The method of successive approximation may be represented symbolically:—

Let the equation for which the particular integral is required be

$$\mathrm{EI}\frac{d^4y}{dx^4}+m\frac{d^2y}{dt^2}=0,$$

subject to end conditions which depend on the moving force P.

Put D for $\frac{d}{dx}$, Δ for $\frac{d}{dt}$, and write k for $-\frac{m}{\mathrm{EI}}$.

Then $$\mathrm{D}^4 y = k\Delta^2 y.$$

The first approximation y_1 is the particular integral of

$$\mathrm{D}^4 y_1 = 0.$$

$$y_2 \text{ is the solution of } \mathrm{D}^4 y_2 = k\Delta^2 y_1,$$

$$y_3 \text{ is the solution of } \mathrm{D}^4 y_3 = k\Delta^2 y_2,$$

$$y_n \text{ is the solution of } \mathrm{D}^4 y_n = k\Delta^2 y_{n-1}.$$

$$\therefore \qquad \begin{aligned} y_n &= \mathrm{D}^{-4} k\Delta^2 y_{n-1}, \\ &= (\mathrm{D}^{-4} k\Delta^2)^2 y_{n-2}, \\ &= (\mathrm{D}^{-4} k\Delta^2)^{n-1} y_1. \end{aligned}$$

Spring-borne mass under action of a fluctuating force.

8. This method of finding the particular integral may be illustrated by the following simple example :—

A mass m is supported by a light spring and is subjected to a fluctuating force $\mathrm{P} = f(t)$.

If y be the deflexion of the spring and k be the force it exerts at unit deflexion, then the equation of motion is

$$m\frac{d^2y}{dt^2} + ky = \mathrm{P}.$$

If, as an example, we choose a simple algebraic variation of P with the time according to the law

$$\mathrm{P} = a + bt + ct^2,$$

the exact solution of this equation is

$$y = \mathrm{A}\sin\left(t\sqrt{\frac{k}{m}} + \gamma\right) + \frac{1}{k}(a + bt + ct^2) - \frac{2mc}{k^2},$$

where A and γ are constants of integration.

The method of successive approximation for finding the particular integral is applied as follows :—

In the equation

$$m\frac{d^2y}{dt^2} + ky = \mathrm{P},$$

first omit the term

$$m\frac{d^2y}{dt^2}.$$

Then $y=\frac{P}{k}$. As this is the result of the first approximation, call this value y_1.

Next substitute this value of y in $m\frac{d^2y}{dt^2}$. which becomes $\frac{2mc}{k}$.

We have now to solve

$$ky+\frac{2mc}{k}=a+bt+ct^2,$$

and the resulting value of y is the second approximation y_2.
We find

$$y_2=\frac{a+bt+ct^2}{k}-\frac{2mc}{k^2}.$$

Proceeding again in like manner with the substitution of y_2 for y in $m\frac{d^2y}{dt^2}$, we obtain the same result, or $y_3=y_2$. In fact, the second approximation has yielded the exact result for the forced vibration.

Spring-borne mass under action of a fluctuating force, including damping.

9. We may take as another example of finding a particular integral that dealt with in paragraph 8, but with the addition of a damping force.

The equation of motion is now of the form

$$m\frac{d^2y}{dt^2}+n\frac{dy}{dt}+ky=P=a+bt+ct^2.$$

Firstly we omit $m\frac{d^2y}{dt^2}+n\frac{dy}{dt}$ and we find $y_1=\frac{a+bt+ct^2}{k}$.

Substitute this value in the terms $m\frac{d^2y}{dt^2}$ and $n\frac{dy}{dt}$, and there results the equation for y_2

$$ky_2+\frac{2mc}{k}+\frac{n}{k}(b+2ct)=a+bt+ct^2,$$

or $$y_2=\frac{1}{k^2}(ak-nb-2mc)+\frac{t}{k^2}(bk-2nc)+\frac{ct^2}{k}.$$

Next put this value of y in the terms $m\frac{d^2y}{dt^2}$ and $n\frac{dy}{dt}$, and we find in like manner

$$y_3=\frac{1}{k^3}(ak^2-2nkc-nkb+2n^2c)+\frac{t}{k^2}(bk-2nc)+\frac{ct^2}{k}.$$

It may readily be verified that this value is exactly the particular integral of the equation.

Light uniform beam with concentrated mass freely supported under action of a fluctuating force.

10. As a further example of this kind consider a massless horizontal beam supported freely at its ends and carrying a mass m fixed at the point $x=x_0$, at which there is applied a force P which varies with the time according to the law

$$\text{P}=a+bt+ct^2.$$

Take the origin at one end of the beam and let the reaction there be R.

We find by taking moments at x,

$$\text{EI}\frac{d^2y}{dx^2}=\text{R}x.$$

Now
$$\text{R}=\left(\text{P}-m\frac{d^2y_0}{dt^2}\right)\frac{l-x_0}{l}.$$

$$\therefore \qquad \text{EI}l\frac{d^2y}{dx^2}=\left(\text{P}-m\frac{d^2y_0}{dt^2}\right)(l-x_0)x.$$

This equation may be solved directly. Thus from 0 to x_0, since $y=0$ at $x=0$,

$$6\text{EI}ly=\left(\text{P}-m\frac{d^2y_0}{dt^2}\right)(l-x_0)x^3+\text{A}x,$$

and in like manner, from x_0 to l, since $y=0$ at $x=l$,

$$6\text{EI}ly'=\left(\text{P}-m\frac{d^2y_0}{dt^2}\right)x_0(l-x)^3+\text{A}'(l-x),$$

where the accent on y indicates that it corresponds to a value of x between x_0 and l.

At
$$x=x_0,\ y=y' \text{ and } \frac{dy}{dx}=\frac{dy'}{dx};$$

hence
$$\text{A}=-\left(\text{P}-m\frac{d^2y_0}{dt^2}\right)x_0(l-x_0)(2l-x_0)$$

and $$A' = -\left(P - m\frac{d^2y_0}{dt^2}\right)x_0(l-x_0)(l+x_0).$$

Hence we obtain

$$6EIly = \left(P - m\frac{d^2y_0}{dt^2}\right)x(l-x_0)(x^2-2lx_0+x_0^2),$$

$$6EIly' = \left(P - m\frac{d^2y_0}{dt^2}\right)x_0(l-x)(x^2-2lx+x_0^2).$$

At $x=x_0$,

$$3EIly_0 = -\left(P - m\frac{d^2y_0}{dt^2}\right)x_0^2(l-x_0)^2.$$

$$\therefore \qquad m\frac{d^2y_0}{dt^2} - \frac{3EIl}{x_0^2(l-x_0)^2}y_0 = P,$$

which is the equation of the forced vibration of an elastic system.

Since $P=a+bt+ct^2$, we can find directly that the particular integral is

$$y_0 = k(a+bt+ct^2) - 2mck^2,$$

where $$k = -\frac{x_0^2(l-x_0)^2}{3EIl}.$$

The complementary function is the solution of

$$m\frac{d^2y_0}{dt^2} + \frac{1}{k}y_0 = 0 \quad \text{or} \quad y_0 = A\sin\left(\frac{t}{\sqrt{km}}+\gamma\right).$$

This represents the free vibration.

The complete solution is therefore

$$y_0 = A\sin\left(\frac{t}{\sqrt{km}}+\gamma\right) - 2mck^2 + k(a+bt+ct^2),$$

where A and γ are arbitrary constants.

We can readily solve this example by the method of successive approximation.

The equation is

$$EIl\frac{d^2y}{dx^2} = \left(P - m\frac{d^2y_0}{dt^2}\right)(l-x_0)x.$$

As a first approximation omit the term $m\frac{d^2y_0}{dt^2}$.

Then $$EIl\frac{d^2y_1}{dx^2} = P(l-x_0)x,$$

$$\therefore \qquad 6EIly_1 = Px(l-x_0)(x^2-2lx_0+x_0^2).$$

$$\therefore \qquad 3\text{EI}l(y_1)_0 = -\text{P}x_0^2(l-x_0)^2;$$

$$\text{or} \qquad (y_1)_0 = k\text{P} = k(a+bt+ct^2).$$

$$\therefore \qquad \frac{d^2(y_1)_0}{dt^2} = 2ck.$$

Substituting this value in the acceleration term, we get a second approximation from the equation

$$\text{EI}l\frac{d^2y_2}{dx^2} = (\text{P}-2mck)(l-x_0)x.$$

$$\therefore \qquad 6\text{EI}ly_2 = (\text{P}-2mck)x(l-x_0)(x^2-2lx_0+x_0^2).$$

$$\therefore \qquad 3\text{EI}l(y_2)_0 = -(\text{P}-2mck)x_0^2(l-x_0)^2.$$

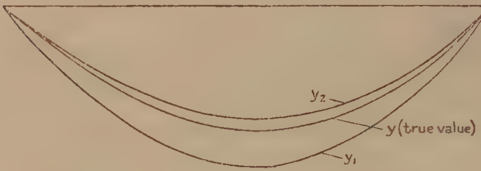
$$\therefore \qquad (y_2)_0 = k\text{P}-2mck^2 = k(a+bt+ct^2)-2mck^2,$$

which agrees exactly with the value of the particular integral obtained above.

Massive uniform beam freely supported under action of a constant force moving uniformly along it.

11. We now proceed to illustrate the application to beams of the method of successive approximation.

Fig. 1.



Here we suppose that throughout the motion the acceleration and damping terms exercise a relatively small influence on the deflexion arising in the forced vibration compared with the applied load, and accordingly a first approximation thereto may be obtained by their omission.

Diagrammatically the sequence of approximations corresponding to a particular time may be represented by fig. 1.

As an example we shall seek a particular integral in the case of a heavy uniform beam supported freely at each end and subjected to a force P of constant magnitude moving with uniform velocity v, gravity and damping being omitted. Let the origin of coordinates be chosen at the end of the beam towards which the force moves, and let x represent the distance measured along the beam, y the deflexion at the point x, l the length of the beam, m the mass of the beam per unit length, I its cross sectional moment of inertia about a line perpendicular to the plane of bending intersecting the neutral axis, E Young's Modulus for the material of the beam.

Let R and R′ represent the reactions of the supports at the origin and other end of the beam respectively when the moving force P is at the position x_0.

Consider the section of the beam at the position x, where $x<x_0$, and let ξ be the running coordinate of any point on the axis of the beam lying between the origin and the position x. Let η be the deflexion at the point ξ.

Taking moments at x we find

$$-\mathrm{EI}l\frac{d^2y}{dx^2}=\mathrm{R}lx+ml\int_0^x(x-\xi)\frac{d^2\eta}{dt^2}d\xi.$$

$$\mathrm{R}l=\mathrm{P}(l-x_0)-m\int_0^{x_0}(l-x)\frac{d^2y}{dt^2}dx-m\int_{x_0}^{l}(l-x)\frac{d^2y'}{dt^2}dx,$$

where the accent on y indicates that it corresponds to a value of x lying between x_0 and l.

Hence between 0 and x_0

$$\mathrm{EI}l\frac{d^2y}{dx^2}=-\mathrm{P}x(l-x_0)+mx\int_0^{x_0}(l-x)\frac{d^2y}{dt^2}dx$$
$$+mx\int_{x_0}^{l}(l-x)\frac{d^2y'}{dt^2}dx-ml\int_0^x(x-\xi)\frac{d^2\eta}{dt^2}d\xi$$

is the equation representing the motion.

To solve this by successive approximations first omit the terms in m. We find that from 0 to x_0

$$y_1=-\frac{\mathrm{P}}{6\mathrm{EI}l}x(l-x_0)(x^2-2lx_0+x_0^2).$$

In like manner, we find from x_0 to l,

$$y_1'=-\frac{\mathrm{P}}{6\mathrm{EI}l}x_0(l-x)(x^2-2lx+x_0^2).$$

Hence $$\frac{d^2y_1}{dt^2}=-\frac{\mathrm{P}v^2}{\mathrm{EI}l}x(l-x_0)$$

and $$\frac{d^2y_1'}{dt^2}=-\frac{\mathrm{P}v^2}{\mathrm{EI}l}x_0(l-x),$$

since $vt=l-x_0$, the zero of time being chosen when the load comes on to the beam at the position $x=l$.

Then

$$\mathrm{EI}l\frac{d^2y_2}{dx^2}=-\mathrm{P}x(l-x_0)-\frac{m\mathrm{P}v^2}{\mathrm{EI}l}x\int_0^{x_0}x(l-x)(l-x_0)dx$$
$$-\frac{m\mathrm{P}v^2}{\mathrm{EI}l}x\int_{x_0}^{l}x_0(l-x)^2dx+\frac{m\mathrm{P}v^2}{\mathrm{EI}}\int_0^{x}\xi(x-\xi)(l-x_0)d\xi.$$

Hence

$$\frac{6\mathrm{E}^2\mathrm{I}^2l}{m\mathrm{P}v^2}\cdot\frac{d^2y_2}{dx^2}$$
$$=-\frac{6\mathrm{EI}}{mv^2}x(l-x_0)-xx_0(l-x_0)(2l-x_0)+x^3(l-x_0).$$

On integration we find

$$\frac{360\mathrm{E}^2\mathrm{I}^2l}{m\mathrm{P}v^2}y_2=-\frac{60\mathrm{EI}}{mv^2}x(l-x_0)(x^2-2lx_0+x_0^2)$$
$$+3x^5(l-x_0)-10x^3x_0(l-x_0)(2l-x_0)+\mathrm{A}x.$$

In like manner we find from x_0 to l

$$\frac{360\mathrm{E}^2\mathrm{I}^2l}{m\mathrm{P}v^2}y_2'=-\frac{60\mathrm{EI}}{mv^2}x_0(l-x)(x^2-2lx+x_0^2)$$
$$+3x_0(l-x)^5-10x_0(l-x)^3(l-x_0)(l+x_0)$$
$$+\mathrm{A}'(l-x).$$

Now at $x=x_0$, $y_2=y_2'$, and $\dfrac{dy_2}{dx}=\dfrac{dy_2'}{dx}$.

Hence we find

$$\mathrm{A}=x_0(l-x_0)(2l-x_0)(4l^2+6lx_0-3x_0^2)$$

and $$\mathrm{A}'=x_0(l-x_0)(l+x_0)(7l^2-3x_0^2).$$

If, now, we write $z=\dfrac{x}{l}$, we have finally from 0 to z_0

$$y_2=-\frac{\mathrm{P}l^3}{6\mathrm{EI}}z(1-z_0)(z^2-2z_0+z_0^2)$$
$$+\frac{m\mathrm{P}v^2l^5}{360\mathrm{E}^2\mathrm{I}^2}[3z^5(1-z_0)-10z^3z_0(1-z_0)(2-z_0)$$
$$+zz_0(1-z_0)(2-z_0)(4+6z_0-3z_0^2)],$$

and from z_0 to 1,

$$y_2'=-\frac{\mathrm{P}l^3}{6\mathrm{EI}}z_0(1-z)(z^2-2z+z_0^2)$$
$$+\frac{m\mathrm{P}v^2l^5}{360\mathrm{E}^2\mathrm{I}^2}[3z_0(1-z)^5-10z_0(1-z)^3(1-z_0)(1+z_0)$$
$$+z_0(1-z)(1-z_0)(1+z_0)(7-3z_0^2)].$$

Similar results would be obtained if, instead of taking the equation of moments as representing the vibratory motion, we had taken

$$\mathrm{EI}\frac{d^4y}{dx^4}+m\frac{d^2y}{dt^2}=0,$$

which may be written down at once or may be obtained from the moments equation by two differentiations with respect to x. The method of successive approximation can be applied to this equation by first omitting the term $m\dfrac{d^2y}{dt^2}$ and solving for y_1, and on substituting this value in that term solving again for y_2. When the constants are determined to fit the conditions of the problem the same value of y_2 results as that already found.

The complete solution of the problem is obtained by finding the complementary function and adding to it the particular integral already obtained.

The solution of

$$\mathrm{EI}\frac{d^4y}{dx^4}+m\frac{d^2y}{dt^2}=0,$$

in which P is now regarded as zero, is readily seen to be of the type

$$y=\mathrm{A}\sin\alpha x\,.\,\sin(\beta t+\gamma),$$

where A and γ are constants of integration and

$$\mathrm{EI}\alpha^4=m\beta^2.$$

Also, since $y=0$ and $\dfrac{d^2y}{dx^2}=0$ at $x=0$ or l, we require $\alpha l=r\pi$ where r is an integer.

Accordingly we obtain

$$y=\Sigma\mathrm{A}_r\sin\frac{r\pi x}{l}\,.\,\sin\left(t\frac{r^2\pi^2}{l^2}\sqrt{\frac{\mathrm{EI}}{m}}+\gamma_r\right):$$

and the complete solution for $z<z_0$ is approximately

$$\begin{aligned}y=\Sigma\mathrm{A}_r\sin r\pi z\,.\,\sin\left(t\frac{r^2\pi^2}{l^2}\sqrt{\frac{\mathrm{EI}}{m}}+\gamma_r\right)&\\ -\frac{\mathrm{P}l^3}{6\mathrm{EI}}z(1-z_0)(z^2-2z_0+z_0^2)&\\ +\frac{m\mathrm{P}v^2l^5}{360\mathrm{E}^2\mathrm{I}^2}[3z^5(1-z_0)-10z^3z_0(1-z_0)(2-z_0)&\\ +zz_0(1-z_0)(2-z_0)(4+6z_0-3z_0^2)].&\end{aligned}$$

Similarly, for $z > z_0$,

$$y' = \Sigma A_r \,.\, \sin r\pi z \,.\, \sin\left(t\frac{r^2\pi^2}{l^2}\sqrt{\frac{EI}{m}} + \gamma_r\right) - \frac{Pl^3}{6EI} z_0(1-z)(z^2-2z+z_0^2)$$
$$+ \frac{mPv^2l^5}{360E^2I^2}[3z_0(1-z)^5 - 10z_0(1-z)^3(1-z_0)(1+z_0) + z_0(1-z)(1-z_0)(1+z_0)(7-3z_0^2)].$$

The constants of integration in the complete solution are to be determined by making the initial state of the beam one of rest, *i. e.*, at $t=0$ we must have $y=0$ and $\frac{dy}{dt}=0$ everywhere throughout it. This can approximately be secured by a suitable choice of the constants.

The tendency of the beam to rupture depends on the extreme fibre stress or strain, and hence on the maximum bending moment to which the beam is subjected.

If the deflexion curve is approximately known throughout the motion, the maximum value of the bending moment can be approximately obtained by the aid of the relation

$$M = EI\frac{d^2y}{dx^2}$$

12. It is worthy of note that this method of finding a particular integral may also be demonstrated in the following manner:—

The value of y that satisfies the differential equation and the boundary conditions at the ends is a function of $\frac{mv^2l^2}{EI}$ and other quantities. Let us suppose y expanded in ascending powers of $\frac{mv^2l^2}{EI}$, thus

$$y = u_0 + u_1\frac{mv^2l^2}{EI} + u_2\left(\frac{mv^2l^2}{EI}\right)^2 + \ldots\ldots$$

We observe that in the problems considered the value of $\frac{mv^2l^2}{EI}$ is small throughout the range involved. Accordingly the terms beyond, say, the second or third in the expansion may be disregarded if their effect on the value of y is negligible throughout the working range.

Now, in the differential equation, substitute for y the value

$$u_0+u_1\frac{mv^2l^2}{\mathrm{EI}}+u_2\left(\frac{mv^2l^2}{\mathrm{EI}}\right)^2+\ldots\ldots,$$

and equate the coefficients of like powers of $\frac{mv^2l^2}{\mathrm{EI}}$ on each side of the equation. This leads to a series of differential equations which we can solve for u_0, u_1, $u_2\ldots$, subject to each of these quantities satisfying the terminal conditions.

Thus we have for u_0 the equation

$$\mathrm{EI}l\frac{d^2u_0}{dx^2}=-\mathrm{P}x(l-x_0),$$

which is the equation already obtained for the first approximation if $u_0=y_1$.

Next, by equating the coefficients of the first power of $\frac{mv^2l^2}{\mathrm{EI}}$, we obtain

$$v^2l^3\frac{d^2u_1}{dx^2}=x\int_0^{x_0}(l-x)\frac{d^2u_0}{dt^2}dx+x\int_{x_0}^{l}(l-x)\frac{d^2u_0'}{dt^2}\,dx$$
$$-l\int_0^x(x-\xi)\frac{d^2w_0}{dt^2}d\xi,$$

where w_0 is the value of u_0 when ξ is written for x in it. This equation gives u_1 since u_0 has already been obtained, and we can readily see that

$$u_0+u_1\frac{mv^2l^2}{\mathrm{EI}}=y_2,$$

where y_2 is the second approximation obtained above.

The next equation leads to u_2, and it is obvious that the method may be carried to such further terms of the approximation as may be desired.

13. Professor Inglis * has given the solution of the problem of paragraph 11 in harmonic series.

For the particular integral he finds

$$y=\frac{2\mathrm{P}l^3}{\pi^4\mathrm{EI}}\left[\frac{\sin\pi z_0\sin\pi z}{1-\dfrac{mv^2l^2}{\pi^2\mathrm{EI}}}+\frac{\sin 2\pi z_0\,.\,\sin 2\pi z}{4\left(4-\dfrac{mv^2l^2}{\pi^2\mathrm{EI}}\right)}+\ldots\right].$$

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* Prof. C. E. Inglis, Min. Proc. Inst. C. E. vol. ccxviii. p. 256 (1924).

Now $\frac{mv^2l^2}{\pi^2\mathrm{EI}}$ is small. Hence, omitting its higher powers than the first, we have approximately

$$y=\frac{2\mathrm{P}l^3}{\pi^4\mathrm{EI}}\left[\sin\pi z_0\,.\,\sin\pi z+\frac{1}{16}\sin 2\pi z_0\sin 2\pi z+\ldots\right]$$

$$+\frac{2m\mathrm{P}v^2l^5}{\pi^6\mathrm{E}^2\mathrm{I}^2}\left[\sin\pi z_0\sin\pi z+\frac{1}{64}\sin 2\pi z_0\sin 2\pi z+\ldots\right].$$

It may easily be verified that this expression gives the same values of y as does that for y_2, for the same values of z and z_0.

Thus if y and y_2 be represented by

$$\frac{\mathrm{P}l^3}{\mathrm{AEI}}+\frac{m\mathrm{P}v^2l^5}{\mathrm{BE}^2\mathrm{I}^2},$$

we find approximately for each solution

$$\mathrm{A}=48,\quad \mathrm{B}=480\quad \text{if } z=z_0=\tfrac{1}{2},$$
$$\mathrm{A}=85{\cdot}3,\quad \mathrm{B}=930{\cdot}9 \text{ if } z=z_0=\tfrac{1}{4},$$
$$\mathrm{A}=69{\cdot}8,\quad \mathrm{B}=680{\cdot}8 \text{ if } z=\tfrac{1}{4},\ z_0=\tfrac{1}{2},$$
$$\mathrm{A}=125{\cdot}4,\quad \mathrm{B}=1140{\cdot}6 \text{ if } z=\tfrac{1}{6},\ z_0=\tfrac{2}{3}.$$

We can, in general, establish the equivalence of the expressions for y_2 and y.

We require to show that

$$-\frac{1}{6}z(1-z_0)(z^2-2z_0+z_0^2)$$

$$=\frac{2}{\pi^4}\left[\sin\pi z_0\sin\pi z+\frac{1}{2^4}\sin 2\pi z_0\sin 2\pi z+\ldots\right],$$

and

$$\frac{1}{360}z(1-z_0)\{3z^4-10z^2z_0(2-z_0)+z_0(2-z_0)(4+6z_0-3z_0^2)\}$$

$$=\frac{2}{\pi^6}\left[\sin\pi z_0\sin\pi z+\frac{1}{2^6}\sin 2\pi z_0\,.\,\sin 2\pi z+\ldots\right],$$

where $$0\ngtr z\ngtr z_0\ngtr 1.$$

Transforming by the substitution

$$2\pi z_0=\theta+\phi,\quad 2\pi z=\theta-\phi,$$

the former becomes

$$\frac{1}{48}\left[\theta^2(\theta-2\pi)^2-\phi^2(\phi-2\pi)^2\right]$$
$$=\cos\phi+\frac{1}{2^4}\cos 2\phi+\frac{1}{3^4}\cos 3\phi+\dots$$
$$-\cos\theta-\frac{1}{2^4}\cos 2\theta-\frac{1}{3^4}\cos 3\theta-\dots.$$

The form of this equation (the validity of which we have to establish) suggests that the function on the left-hand side, which is an even one in θ and ϕ, should be developed in a Fourier's series of cosines. Let it be represented by f and be regarded as a function of θ for any constant value of ϕ.

Let $f=a_0+a_1\cos\theta+a_2\cos 2\theta+\dots+a_n\cos n\theta+\dots.$

Then, following the usual method of Fourier's expansion, multiply both sides by $\cos n\theta\, d\theta$ and integrate between the limits 0 and π.

$$\therefore \qquad \int_0^\pi f\,.\cos n\theta\,.\,d\theta=\frac{\pi}{2}a_n.$$

Multiply both sides by $d\theta$ and integrate between 0 and π.

$$\therefore \qquad \int_0^\pi f\,.\,d\theta=\pi a_0.$$

The several coefficients a_0, a_1, a_2, etc. in the expansion can thus be found.

Now, if we integrate by parts the expression

$$\int^\pi f\,.\cos n\theta\, d\theta,$$

we obtain

$$\Big|_0^\pi \frac{f}{n}\sin n\theta+\int_0^\pi\frac{f'}{n}\sin n\theta\, d\theta,$$

where f' stands for $\frac{df}{d\theta}$. Proceeding step by step in this manner, we obtain

$$\int_0^\pi f\,.\cos n\theta\,.\,d\theta=\Big|_0^\pi\frac{f}{n}\sin n\theta+\Big|_0^\pi\frac{f'}{n^2}\cos n\theta-\Big|_0^\pi\frac{f''}{n^3}\sin n\theta$$
$$-\Big|_0^\pi\frac{f'''}{n^4}\cos n\theta+\Big|_0^\pi\frac{f^{\text{iv}}}{n^5}\sin n\theta+\dots.$$

But $$\Big|_0^\pi \frac{f}{n}\sin n\theta = 0, \quad \Big|_0^\pi \frac{f''}{n^3}\sin n\theta = 0, \text{ etc.,}$$

since $\sin n\pi = 0$.

$$\therefore \int_0^\pi f\,.\cos n\theta\,.\,d\theta = \Big|_0^\pi \cos n\theta\,.\left\{\frac{f'}{n^2} - \frac{f'''}{n^4} + \frac{f^{\mathrm{v}}}{n^6} - \dots\right\}.$$

In the present case

$$f' = \frac{1}{12}\theta(\theta-\pi)(\theta-2\pi)$$

$$f''' = \frac{1}{2}(\theta-\pi).$$

$$f^{\mathrm{v}} = 0, \text{ etc.}$$

Accordingly

$$a_n = \frac{2}{\pi}\Big|_0^\pi \cos n\theta\left\{\frac{f'}{n^2} - \frac{f'''}{n^4} + \frac{f^{\mathrm{v}}}{n^6} - \dots\right\}$$

$$= -\frac{1}{n^4}.$$

Also

$$a_0 = \frac{1}{\pi}\int_0^\pi f\,d\theta = \frac{1}{90}\pi^4 - \frac{1}{48}\phi^2(\phi-2\pi)^2.$$

Hence

$$f = \frac{1}{90}\pi^4 - \frac{1}{48}\phi^2(\phi-2\pi)^2 - \frac{\cos\theta}{1^4} - \frac{\cos 2\theta}{2^4} - \dots.$$

In like manner, regarding θ as constant and ϕ as variable, we have

$$-f = \frac{\pi^4}{90} - \frac{1}{48}\theta^2(\theta-2\pi)^2 - \frac{\cos\phi}{1^4} - \frac{\cos 2\phi}{2^4} - \dots.$$

Subtracting this result from the preceding we find

$$f = \frac{1}{48}\{\theta^2(\theta-2\pi)^2 - \phi^2(\phi-2\pi)^2\}$$

$$= \frac{\cos\phi}{1^4} + \frac{\cos 2\phi}{2^4} + \dots - \frac{\cos\theta}{1^4} - \frac{\cos 2\theta}{2^4} - \dots,$$

which establishes the identity of the expressions within the usual limits.

The equivalence of the second expressions can be established in a similar manner. With the same transformation, and after reduction, we have to show that f, or

$$\frac{1}{1440}\left[\theta^2(\theta^4-6\pi\theta^3+10\pi^2\theta^2-8\pi^4)\right.$$
$$\left.-\phi^2(\phi^4-6\pi\phi^3+10\pi^2\phi^2-8\pi^4)\right]$$
$$=\frac{\cos\theta}{1^6}+\frac{\cos 2\theta}{2^6}+\ldots-\frac{\cos\phi}{1^6}-\frac{\cos 2\phi}{2^6}-\ldots.$$

Proceeding exactly as before, we find

$$a_n=\frac{1}{n^6}.$$

$$a_0=-\frac{\pi^6}{945}-\frac{1}{1440}\phi^2(\phi^4-6\pi\phi^3+10\pi^2\phi^2-8\pi^4).$$

$$\therefore\quad f=-\frac{\pi^6}{945}-\frac{1}{1440}\phi^2(\phi^4-6\pi\phi^3+10\pi^2\phi^2-8\pi^4)$$
$$+\frac{\cos\theta}{1^6}+\frac{\cos 2\theta}{2^6}+\ldots.$$

Also

$$f=\frac{\pi^6}{945}+\frac{1}{1440}\theta^2(\theta^4-6\pi\theta^3+10\pi^2\theta^2-8\pi^4)$$
$$-\frac{\cos\phi}{1^6}-\frac{\cos 2\phi}{2^6}-\ldots.$$

Hence

$$f=\frac{\cos\theta}{1^6}+\frac{\cos 2\theta}{2^6}+\ldots-\frac{\cos\phi}{1^6}-\frac{\cos 2\phi}{2^6}-\ldots,$$

thus establishing the identity of the second expressions within the usual limits.

Thus $y_2=y$ within the limits of the problem.

Massive uniform beam freely supported under action of a fluctuating force moving uniformly along it.

14. If, in the example of paragraph 11, the uniformly moving force is not constant but varies with the time according to any given law, the same method may be employed for finding approximately a particular integral.

We find the same values of y_1 and y_1' as in paragraph 11, but we observe that $\frac{d^2y_1}{dt^2}$ and $\frac{d^2y_1'}{dt^2}$ now include terms involving $\dot{P}$ and $\ddot{P}$ in addition to those in P, where $\dot{P}$ and $\ddot{P}$ stand for $\frac{dP}{dt}$ and $\frac{d^2P}{dt^2}$ according to the usual notation.

With this addition we proceed precisely as in paragraph **11**, and obtain, finally, the following values of y_2 and y_2' :—

$$\begin{aligned}
15120\,\mathrm{E}^2\mathrm{I}^2 y_2 = {} & 2520\,\mathrm{EIP}l^3 z(1-z_0)\{z_0(2-z_0)-z^2\} \\
& + 42m\mathrm{P}v^2 l^5 z(1-z_0)[z_0(2-z_0)(4+6z_0-3z_0^2) \\
& \qquad\qquad -10z^2 z_0(2-z_0)+3z^4] \\
& + 2m\dot{\mathrm{P}}vl^6 z[32-168z_0^2+210z_0^4-126z_0^5+21z_0^6 \\
& \quad -7z^2(8-60z_0^2+60z_0^3-15z_0^4)+21z^4(2-6z_0+3z_0^2) \\
& \qquad\qquad +3z^6] \\
& - m\ddot{\mathrm{P}}l^7 z(1-z_0)[z_0(2-z_0)(16+24z_0-12z_0^3+3z_0^4) \\
& \quad -7z^2 z_0(2-z_0)(4+6z_0-3z_0^2)+21z^4 z_0(2-z_0)-3z^6].
\end{aligned}$$

$$\begin{aligned}
15120\,\mathrm{E}^2\mathrm{I}^2 y_2' = {} & 2520\,\mathrm{EIP}l^3 z_0(1-z)\{1-z_0^2-(1-z)^2\} \\
& + 42m\mathrm{P}v^2 l^5 z_0(1-z)[(1-z_0^2)(7-3z_0^2) \\
& \qquad\qquad -10(1-z)^2(1-z_0^2)+3(1-z)^4] \\
& + 2m\dot{\mathrm{P}}vl^6(1-z)[31-147z_0^2+105z_0^4-21z_0^6 \\
& \quad -7(1-z)^2(7-30z_0^2+15z_0^4)+21(1-z)^4(1-3z_0^2) \\
& \qquad\qquad -3(1-z)^6] \\
& - m\mathrm{P}l^7 z_0(1-z)[(1-z_0^2)(31-18z_0^2+3z_0^4) \\
& \quad -7(1-z)^2(1-z_0^2)(7-3z_0^2)+21(1-z)^4(1-z_0^2) \\
& \qquad\qquad -3(1-z)^6].
\end{aligned}$$

Tables may be prepared or curves plotted for the functions of position involved in these values to facilitate computation in their application.

In particular, the uniformly moving force P may be made up of a constant part and of another part varying as a harmonic function of the time representing the vertical component of an unbalanced centrifugal force. Thus P takes the form $p+q\sin(ct+\alpha)$. The solution of this important particular case is obviously included in the more general results just obtained, and may be deduced therefrom by the substitutions

$$\mathrm{P}=p+q\sin(ct+\alpha), \qquad \dot{\mathrm{P}}=qc\cos(ct+\alpha),$$
$$\mathrm{P}=-qc^2\sin(ct+\alpha).$$

Massless uniform beam freely supported under action of a mass moving uniformly along it.

15. As another example we shall consider a uniform massless horizontal beam freely supported at its ends and

subjected to the action of a single mass M moving along it with uniform velocity v, disregarding damping.

Taking the origin at the end of the beam towards which the mass is moving, we have, by taking moments for $x < x_0$,

$$\mathrm{EI}\frac{d^2y}{dx^2}=\mathrm{R}x,$$

where R is the reaction of the support at the origin.

$$\mathrm{R}l=\mathrm{M}(l-x_0)\left(g-\frac{d^2y_0}{dt^2}\right).$$

Hence $$\frac{d^2y}{dx^2}=\frac{\mathrm{M}}{\mathrm{EI}l}(l-x_0)x\left(g-\frac{d^2y_0}{dt^2}\right).$$

As a first approximation omit $\frac{d^2y_0}{dt^2}$ and we have for $x<x_0$

$$\frac{d^2y_1}{dx^2}=\frac{\mathrm{M}g}{\mathrm{EI}l}(l-x_0)x.$$

Hence $$y_1=\frac{\mathrm{M}g}{6\mathrm{EI}l}(l-x_0)x^3+\mathrm{A}x.$$

For $x>x_0$ we find in like manner

$$y_1'=\frac{\mathrm{M}g}{6\mathrm{EI}l}x_0(l-x)^3+\mathrm{A}'(l-x).$$

At $x=x_0$, $y_1=y_1'$, and $\frac{dy_1}{dx}=\frac{dy_1'}{dx}$, hence

$$\mathrm{A}=-\frac{\mathrm{M}g}{6\mathrm{EI}l}x_0(l-x_0)(2l-x_0)$$

and $$\mathrm{A}'=-\frac{\mathrm{M}g}{6\mathrm{EI}l}x_0(l-x_0)(l+x_0).$$

Hence $$y_1=\frac{\mathrm{M}g}{6\mathrm{EI}l}x(l-x_0)(x^2-2lx_0+x_0^2)$$

$$y_1'=\frac{\mathrm{M}g}{6\mathrm{EI}l}x_0(l-x)(x^2-2lx+x_0^2).$$

For a second approximation we have for $x<x_0$

$$\frac{d^2y_2}{dx^2}=\frac{\mathrm{M}}{\mathrm{EI}l}x(l-x_0)\left\{g-\frac{d^2(y_1)_0}{dt^2}\right\}.$$

Now $x_0=l-vt$.

$$\therefore\quad\frac{d^2y_2}{dx^2}=\frac{\mathrm{M}g}{3\mathrm{EI}l}x(l-x_0)\left[3+\frac{2\mathrm{M}v^2}{\mathrm{EI}l}(l^2-6lx_0+6x_0^2)\right].$$

The solution of this equation is

$$y_2=\frac{Mg}{6EIl}x^3(l-x_0)+\frac{M^2v^2g}{9E^2I^2l^2}x^3(l-x_0)(l^2-6lx_0+6x_0^2)$$
$$+Bx.$$

In like manner for $x>x_0$ we find

$$y_2'=\frac{Mg}{6EIl}x_0(l-x)^3+\frac{M^2v^2g}{9E^2I^2l^2}x_0(l-x)^3(l^2-6lx_0+6x_0^2)$$
$$+B'(l-x).$$

Now, at $x=x_0$, we have

$$y_2=y_2' \quad\text{and}\quad \frac{dy_2}{dx}=\frac{dy_2'}{dx},$$

hence

$$B=-\frac{Mg}{6EIl}x_0(l-x_0)(2l-x_0)$$
$$-\frac{M^2v^2g}{9E^2I^2l^2}x_0(l-x_0)(2l-x_0)(l^2-6lx_0+6x_0^2),$$

$$B'=-\frac{Mg}{6EIl}x_0(l-x_0)(l+x_0)$$
$$-\frac{M^2v^2g}{9E^2I^2l^2}x_0(l-x_0)(l+x_0)(l^2-6lx_0+6x_0^2).$$

Hence

$$y_2=\frac{Mg}{6EIl}x(l-x_0)(x^2-2lx_0+x_0^2)$$
$$+\frac{M^2v^2g}{9E^2I^2l^2}x(l-x_0)(x-2lx_0+x_0^2)(l^2-6lx_0+6x_0^2)$$

and

$$y_2'=\frac{Mg}{6EIl}x_0(l-x)(x^2-2lx+x_0^2)$$
$$+\frac{M^2v^2g}{9E^2I^2l^2}x_0(l-x)(x^2-2lx+x_0^2)(l^2-6lx_0+6x_0^2).$$

We may proceed in like manner to a third approximation and obtain the following results:

$$y_3=y_2+\frac{2M^3v^4g}{27E^3I^3l^3}x(l-x_0)(x^2-2lx_0+x_0^2)$$
$$(l^4-24l^3x_0+114l^2x_0^2-180lx_0^3+90x_0^4)$$

and

$$y_3'=y_2'+\frac{2M^3v^4g}{27E^3I^3l^3}x_0(l-x)(x^2-2lx+x_0^2)$$
$$(l^4-24l^3x_0+114l^2x_0^2-180lx_0^3+90x_0^4).$$

It will be observed that for a given position of the load the value of $\frac{y_2-y_1}{y_1}$ at any point is proportional to $\frac{Mv^2l}{EI}$, and $\frac{y_3-y_2}{y_1}$ is proportional to $\left(\frac{Mv^2l}{EI}\right)^2$. As the quantity $\frac{Mv^2l}{EI}$ is small in the problems here considered, the approximations are rapidly convergent and the second approximation is usually sufficient.

Massive uniform beam freely supported under action of a mass moving uniformly along it, including damping.

16. We now turn to the solution of a more difficult problem not hitherto solved in general terms.

Professor Timoshenko has* stated that "the problem of forced vibration produced in beams by rolling masses was more difficult than those relating to vibrations produced by moving forces, and so far a satisfactory method of solving this kind of problem had not been found."

Required to find the vibrations of a heavy uniform beam of mass m per unit length supported freely at each end, the supports being in the same horizontal plane, under the action of a mass M moving with uniform velocity v along it, subject to damping.

Following generally the same notation as in paragraph 11 and taking moments in like manner, we find for $x<x_0$:

$$\begin{aligned}\mathrm{EI}l\frac{d^2y}{dx^2} = & -\mathrm{M}x(l-x_0)\left(g-\frac{d^2y_0}{dt^2}\right)+mx\int_0^{x_0}(l-x)\frac{d^2y}{dt^2}dx \\ & +mx\int_{x_0}^{l}(l-x)\frac{d^2y'}{dt^2}dx+\tfrac{1}{2}mg\,lx^2-\tfrac{1}{2}mg\,l^2x \\ & -ml\int_0^{x}(x-\xi)\frac{d^2\eta}{dt^2}d\xi+bx\int_0^{x_0}(l-x)\frac{dy}{dt}dx \\ & +bx\int_{x_0}^{l}(l-x)\frac{dy'}{dt}dx-bl\int_0^{x}(x-\xi)\frac{d\eta}{dt}d\xi,\end{aligned}$$

where b is the coefficient of damping and the force exerted by M on the beam is represented by

$$\mathrm{M}\left(g-\frac{d^2y_0}{dt^2}\right).$$

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* Prof. S. P. Timoshenko, Min. Proc. Inst. C. E. vol. ccxviii. p. 314 (1924).

We regard the beam as executing a forced vibration under the action of this force, of which the magnitude depends to a small extent on the value of the deflexion.

In a first approximation we omit the damping and acceleration terms and obtain

$$\frac{\mathrm{EI}l}{g}\frac{d^2y_1}{dx^2}=-\mathrm{M}(l-x_0)x+\tfrac{1}{2}mlx^2-\tfrac{1}{2}ml^2x.$$

Hence for $x<x_0$

$$\frac{24\mathrm{EI}l}{g}y_1=-4\mathrm{M}x^3(l-x_0)-mlx^3(2l-x)+\mathrm{A}x.$$

In like manner for $x>x_0$

$$\frac{24\mathrm{EI}l}{g}y_1'=-4\mathrm{M}x_0(l-x)^3-ml(l-x)^3(l+x)+\mathrm{A}'(l-x).$$

Now, at $x=x_0$, we have $y_1=y_1'$ and $\frac{dy_1}{dx}=\frac{dy_1'}{dx}$, since the beam is continuous there; hence we find

$$\mathrm{A}\ =4\mathrm{M}x_0(l-x_0)(2l-x_0)+ml^4,$$
$$\mathrm{A}'=4\mathrm{M}x_0(l-x_0)(l+x_0)+ml^4.$$

Hence for $x<x_0$

$$\frac{24\mathrm{EI}l}{g}y_1=-4\mathrm{M}x(l-x_0)(x^2-2lx_0+x_0^2)$$
$$+mlx(l-x)(l^2+lx-x^2),$$

and for $x>x_0$

$$\frac{24\mathrm{EI}l}{g}y_1'=-4\mathrm{M}x_0(l-x)(a^2-2lx+x_0^2)$$
$$+mlx(l-x)(l^2+lx-x^2).$$

We proceed now to find the complementary function or the free vibration of the beam which is obtained from the general equation by omitting the term containing M. For convenience this is given separately in the next paragraph (§ 17).

Let y_0'' be the value of the complementary function at x_0.

For the second approximation we substitute y_1 (and y_1') for y in the acceleration terms in m and in the damping terms, and substitute $(y_1)_0+y_0''$ for y_0 in the term in M.

Note that $x_0=l-vt$, and let θ stand for $1-\frac{1}{g}\cdot\frac{d^2y_0''}{dt^2}$.

We have

$$\frac{6\mathrm{EI}l}{g}\cdot\frac{dy_1}{dt}=-\mathrm{M}vx(2l^2-6lx_0+3x_0{}^2+x^2)$$

$$\frac{\mathrm{EI}l}{g}\cdot\frac{d^2y_1}{dt^2}=-\mathrm{M}v^2x(l-x_0)$$

$$\frac{6\mathrm{EI}l}{g}\cdot\frac{d^2(y_1)_0}{dt^2}=\frac{6\mathrm{EI}l}{g}\cdot\frac{d^2(y_1{}')_0}{dt^2}=4\mathrm{M}v^2(l^2-6lx_0+6x_0{}^2)$$
$$-3mv^2lx_0(l-x_0)$$

$$\frac{6\mathrm{EI}l}{g}\cdot\frac{dy_1{}'}{dt}=\mathrm{M}v(l-x)(x^2-2lx+3x_0{}^2)$$

$$\frac{\mathrm{EI}l}{g}\cdot\frac{d^2y_1{}'}{dt^2}=-\mathrm{M}v^2x_0(l-x).$$

We substitute these values in the acceleration and damping terms, and thus obtain the following equation for y_2, which is a second approximation;

$$\begin{aligned}\frac{6\mathrm{E}^2\mathrm{I}^2l^2}{g}\cdot\frac{d^2y_2}{dx^2}=&-3\mathrm{EI}lx\{2\mathrm{M}\theta(l-x_0)+ml(l-x)\}\\&+\mathrm{M}v^2x(l-x_0)\{4\mathrm{M}(l^2-6lx_0+6x_0{}^2)-3mlx_0(l-x_0)\}\\&-6\mathrm{M}mv^2x(l-x_0)\int_0^{x_0}x(l-x)\,dx\\&-6\mathrm{M}mv^2xx_0\int_{x_0}^{l}(l-x)^2\,dx\\&+6\mathrm{M}mv^2l(l-x_0)\int_0^{x}(x-\xi)\,\xi\,d\xi\\&-b\mathrm{M}vx\int_0^{x_0}x(l-x)(2l^2-6lx_0+3x_0{}^2+x^2)\,dx\\&+b\mathrm{M}vx\int_{x_0}^{l}(l-x)^2(x^2-2lx+3x_0{}^2)\,dx\\&+b\mathrm{M}vl\int_0^{x}\xi(x-\xi)(2l^2-6lx_0+3x_0{}^2+\xi^2)\,d\xi.\end{aligned}$$

Performing the integrations and reducing, we find

$$\begin{aligned}\frac{360\mathrm{E}^2\mathrm{I}^2l^2}{g}\cdot\frac{d^2y_2}{dx^2}=&-180\mathrm{EI}\,lx\{2\mathrm{M}\theta(l-x_0)+ml(l-x)\}\\&+240\mathrm{M}^2v^2x(l-x_0)(l^2-6lx_0+6x_0{}^2)\\&-60\mathrm{M}mv^2lx(l-x_0)(5lx_0-4x_0{}^2-x^2)\\&-b\mathrm{M}vlx\{8l^4-60l^2x_0{}^2+60lx_0{}^3-15x_0{}^4\\&\qquad-10x^2(2l^2-6lx_0+3x_0{}^2)-3x^4\}.\end{aligned}$$

Hence on integration

$$\begin{aligned}\frac{360\mathrm{E}^2\mathrm{I}^2l^2}{g}\cdot y_2 = &-60\mathrm{EIM}l\theta x^3(l-x_0)-15\mathrm{EI}ml^2x^3(2l-x)\\ &+40\mathrm{M}^2v^2x^3(l-x_0)(l^2-6lx_0+6x_0^2)\\ &-\mathrm{M}mv^2lx^3(l-x_0)\{10x_0(5l-4x_0)-3x^2\}\\ &-\frac{b}{42}\mathrm{M}vlx^3\{7(8l^4-60l^2x_0^2+60lx_0^3-15x_0^4)\\ &\qquad\qquad-21x^2(2l^2-6lx_0+3x_0^2)-3x^4\}\\ &+\mathrm{B}x.\end{aligned}$$

In like manner we find

$$\begin{aligned}\frac{360\mathrm{E}^2\mathrm{I}^2l^2}{g}\cdot y_2' = &-60\mathrm{EIM}l\theta x_0(l-x)^3-15\mathrm{EI}ml^2(l-x)^3(l+x)\\ &+40\mathrm{M}^2v^2x_0(l-x)^3(l^2-6lx_0+6x_0^2)\\ &-\mathrm{M}mv^2lx_0(l-x)^3\{10(l-x_0)(l+4x_0)-3(l-x)^2\}\\ &-\frac{b}{42}\mathrm{M}vl(l-x)^3\{7(7l^4-30l^2x_0^2+15x_0^4)\\ &\qquad\qquad-21(l-x)^2(l^2-3x_0^2)+3(l-x)^4\}\\ &+\mathrm{B}'(l-x).\end{aligned}$$

Now at $x=x_0$ we have $y_2=y_2'$ and $\frac{dy_2}{dx}=\frac{dy_2'}{dx}$, hence we find

$$\begin{aligned}\mathrm{B} = {}&60\mathrm{EIM}l\theta x_0(l-x_0)(2l-x_0)+15\mathrm{EI}ml^5\\ &-40\mathrm{M}^2v^2x_0(l-x_0)(2l-x_0)(l^2-6lx_0+6x_0^2)\\ &+\mathrm{M}mv^2lx_0(l-x_0)\{8l^3+68l^2x_0-102lx_0^2+33x_0^3\}\\ &+\frac{b}{42}\mathrm{M}vl\{32l^6-168l^4x_0^2+210l^2x_0^4-126lx_0^5+21x_0^6\}\end{aligned}$$

and

$$\begin{aligned}\mathrm{B}' = {}&60\mathrm{EIM}l\theta x_0(l-x_0)(l+x_0)+15\mathrm{EI}ml^5\\ &-40\mathrm{M}^2v^2x_0(l-x_0)(l+x_0)(l^2-6lx_0+6x_0^2)\\ &+\mathrm{M}mv^2lx_0(l-x_0)\{7l^3+37l^2x_0-3lx_0^2-33x_0^3\}\\ &+\frac{b}{42}\mathrm{M}vl\{31l^6-147l^4x_0^2+105l^2x_0^4-21x_0^6\}.\end{aligned}$$

Substituting these values, we obtain, for $x<x_0$,

$$\begin{aligned}\frac{360\mathrm{E}^2\mathrm{I}^2l^2}{g}\cdot y_2 = &-60\mathrm{EIM}l\theta x(l-x_0)(x^2-2lx_0+x_0^2)\\ &+15\mathrm{EI}ml^2x(l-x)(l^2+lx-x^2)\end{aligned}$$

$$
\begin{aligned}
&+40M^2v^2x(l-x_0)(l^2-6lx_0+6x_0^2)(x^2-2lx_0+x_0^2)\\
&+Mmv^2lx(l-x_0)\{3x^4-10x^2x_0(5l-4x_0)\\
&\qquad\qquad+x_0(8l^3+68l^2x_0-102lx_0^2+33x_0^3)\}\\
&+\frac{b}{42}Mvlx\{3x^6+21x^4(2l^2-6lx_0+3x_0^2)\\
&\qquad-7x^2(8l^4-60l^2x_0^2+60lx_0^3-15x_0^4)\\
&\qquad+32l^6-168l^4x_0^2+210l^2x_0^4-126lx_0^5+21x_0^6\},
\end{aligned}
$$

and for $x > x_0$

$$
\begin{aligned}
\frac{360E^2I^2l^2}{g}\cdot y_2' &= -60EIMl\theta x_0(l-x)(x^2-2lx+x_0^2)\\
&+15EIml^2x(l-x)(l^2+lx-x^2)\\
&+40M^2v^2x_0(l-x)(l^2-6lx_0+6x_0^2)(x^2-2lx+x_0^2)\\
&+Mmv^2lx_0(l-x)\{3(l-x)^4-10(l-x)^2(l-x_0)(l+4x_0)\\
&\qquad+(l-x_0)(7l^3+37l^2x_0-3lx_0^2-33x_0^3)\}\\
&-\frac{b}{42}Mvl(l-x)\{3(l-x)^6-21(l-x)^4(l^2-3x_0^2)\\
&\qquad+7(l-x)^2(7l^4-30l^2x_0^2-15x_0^4)\\
&\qquad-31l^6+147l^4x_0^2-105l^2x_0^4+21x_0^6\}.
\end{aligned}
$$

Finally, if we put $z=\frac{x}{l}$, we have for $z<z_0$,

$$
\begin{aligned}
\frac{360E^2I^2}{gl^3}\cdot y_2 &= EIM\theta f_1(z, z_0)+EImlf_2(z, z_0)\\
&+M^2v^2l\phi(z, z_0)+Mmv^2l^2\psi(z, z_0)\\
&+bMvl^3\chi(z, z_0),
\end{aligned}
$$

where

$$
\begin{aligned}
f_1(z, z_0) &= -60z(1-z_0)(z^2-2z_0+z_0^2)\\
f_2(z, z_0) &= 15z(1-z)(1+z-z^2)\\
\phi(z, z_0) &= 40z(1-z_0)(1-6z_0+6z_0^2)(z^2-2z_0+z_0^2)\\
\psi(z, z_0) &= z(1-z_0)\{3z^4-10z^2z_0(5-4z_0)\\
&\qquad+z_0(8+68z_0-102z_0^2+33z_0^3)\}\\
\chi(z, z_0) &= \frac{z}{42}\{3z^6+21z^4(2-6z_0+3z_0^2)\\
&\qquad-7z^2(8-60z_0^2+60z_0^3-15z_0^4)\\
&\qquad+32-168z_0^2+210z_0^4-126z_0^5+21z_0^6\},
\end{aligned}
$$

and for $z > z_0$

$$\frac{360\mathrm{E}^2\mathrm{I}^2}{gl^3} \cdot y_2' = \mathrm{EIM}\theta f_1'(z, z_0) + \mathrm{EI}mlf_2(z, z_0)$$
$$+ \mathrm{M}^2v^2l\phi'(z, z_0) + \mathrm{M}mv^2l^2\psi'(z, z_0)$$
$$+ b\mathrm{M}vl^3\chi'(z, z_0),$$

where

$$f_1'(z, z_0) = -60z_0(1-z)(z^2-2z+z_0^2)$$
$$f_2(z, z_0) = 15z(1-z)(1+z-z^2)$$
$$\phi'(z, z_0) = 40z_0(1-z)(1-6z_0+6z_0^2)(z^2-2z+z_0^2)$$
$$\psi'(z, z_0) = z_0(1-z)\{3(1-z)^4-10(1-z)^2(1-z_0)(1+4z_0)$$
$$+(1-z_0)(7+37z_0-3z_0^2-33z_0^3)\}$$
$$\chi'(z, z_0) = -\frac{1-z}{42}\{3(1-z)^6-21(1-z)^4(1-3z_0^2)$$
$$+7(1-z)^2(7-30z_0^2+15z_0^4)$$
$$-31+147z_0^2-105z_0^4+21z_0^6\}.$$

Computation of arithmetical values can be greatly facilitated by the use of tables constructed, or curves plotted, to represent the algebraic functions of the positions z, z_0, viz.:—f_1, f_2, ϕ, ψ, χ, and f_1', ϕ', ψ', χ'. When these functions of position have been tabulated or plotted once for all, we have only to form the products indicated in any particular example.

17. We now proceed to find the complementary function (which represents the free vibration after the moving load has passed off the beam) and thus the complete solution.

The complementary function is the solution of the general equation in which M is omitted, or of

$$\mathrm{EI}l\frac{d^2y}{dx^2} = -\tfrac{1}{2}mglx(l-x) + mx\int_0^l (l-x)\frac{d^2y}{dt^2}\,dx$$
$$-ml\int_0^x (x-\xi)\frac{d^2\eta}{dt^2}\,d\xi + bx\int_0^l (l-x)\frac{dy}{dt}\,dx$$
$$-bl\int_0^x (x-\xi)\frac{d\eta}{dt}\,d\xi.$$

This equation, on being differentiated twice with respect to x, becomes

$$\mathrm{EI}\frac{d^4y}{dx^4} + m\frac{d^2y}{dt^2} + b\frac{dy}{dt} = mg.$$

The solution of this equation is

$$y'' = \Sigma \mathrm{A} e^{-nt} . \sin px . \sin (qt+\gamma) + \frac{mg}{24\mathrm{EI}} x(l-x)(l^2+lx-x^2).$$

The last term is the gravitational deflexion, and we observe accordingly that the free vibration takes place about the gravitationally deflected position. With this proviso we may omit the term in mg from the equation, as it has been included in paragraph 16.

In order that this value of y shall hold good at all values of t, we require

$$n = \frac{b}{2m}$$

and

$$q^2 = \frac{p^4 \mathrm{EI}}{m} - \frac{b^2}{4m^2}.$$

Also, to satisfy the end conditions, we require

$$p = \frac{r\pi}{l},$$

where r is an integer. A and γ are arbitrary constants and are determined by the initial conditions that at $t=0$ we have $y=0$ and $\dfrac{dy}{dt}=0$ for all values of x if the gravitational deflexion be omitted.

We now find that the value of θ is given by

$$\theta = 1 + \frac{1}{g} \Sigma \mathrm{A} e^{-\frac{bl(1-z_0)}{2mv}}$$

$$\left[\left(\frac{r^2\pi^2v^2}{l^2} + q^2 - \frac{b^2}{4m^2}\right) . \sin r\pi z_0 . \sin \left\{ \frac{ql}{v}(1-z_0) + \gamma \right\}\right.$$

$$- \frac{r\pi vb}{lm} . \cos r\pi z_0 . \sin \left\{ \frac{ql}{v}(1-z_0) + \gamma \right\}$$

$$+ \frac{qb}{m} . \sin r\pi z_c . \cos \left\{ \frac{ql}{v}(1-z_0) + \gamma \right\}$$

$$\left. + \frac{2r\pi vq}{l} . \cos r\pi z_0 . \cos \left\{ \frac{ql}{v}(1-z_0) + \gamma \right\} \right].$$

The complete solution for $z<z_0$ is

$$y=\Sigma \mathrm{A}_r e^{-\frac{bl(1-z_0)}{2mv}}.\sin r\pi z.\sin\left\{\frac{ql}{v}(1-z_0)+\gamma_r\right\}$$

$$+\frac{\mathrm{M}gl^3\theta}{360\mathrm{EI}}f_1(z,z_0)+\frac{mgl^4}{360\mathrm{EI}}f_2(z,z_0)$$

$$+\frac{\mathrm{M}^2v^2gl^4}{360\mathrm{E}^2\mathrm{I}^2}\phi(z,z_0)+\frac{\mathrm{M}mv^2gl^5}{360\mathrm{E}^2\mathrm{I}^2}\psi(z,z_0)$$

$$+\frac{b\mathrm{M}vgl^6}{360\mathrm{E}^2\mathrm{I}^2}\chi(z,z_0),$$

where

$$q^2=\frac{r^4\pi^4\mathrm{EI}}{ml^4}-\frac{b^2}{4m^2},$$

r is an integer, and $l(1-z_0)=vt$.

Similarly for $z>z_0$.

When $t=0$, we have

$$y=\Sigma \mathrm{A}_r.\sin\gamma_r.\sin r\pi z+\frac{mgl^4}{24\mathrm{EI}}z(1-z)(1+z-z^2)$$

$$+\frac{b\mathrm{M}gvl^6}{15120\mathrm{E}^2\mathrm{I}^2}z(3z^6-21z^4+49z^2-31),$$

and, omitting the gravitational deflexion, we require to choose the A sin γ values so that

$$\Sigma \mathrm{A}_r.\sin\gamma_r.\sin r\pi z$$

$$=\frac{b\mathrm{M}gvl^6}{15120\mathrm{E}^2\mathrm{I}^2}z(31-49z^2+21z^4-3z^6).$$

Also, when $t=0$, $\frac{dy}{dt}=0$, hence

$$\Sigma \mathrm{A}_r\left(\frac{b}{2m}\sin\gamma_r-q\cos\gamma_r\right).\left\{\sin r\pi z+\frac{r\pi \mathrm{M}v^2lz(1-z^2)}{3\mathrm{EI}}\right\}$$

$$=\frac{\mathrm{M}vgl^2z(1-z^2)}{360\mathrm{E}^2\mathrm{I}^2}\{60\mathrm{EI}-40\mathrm{M}v^2l+mv^2l^2(7-3z^2)\}$$

The A sin γ and A cos γ values are also to be chosen to satisfy this equation.

Thus as an approximation if when $t=0$ we simply make y equal to the gravitational deflexion and $\frac{dy}{dt}=0$ at the middle point of the beam $z=\frac{1}{2}$, then

$$\mathrm{A}\sin\gamma=\frac{61b\mathrm{M}vgl^6}{92160\mathrm{E}^2\mathrm{I}^2}$$

and

$$\mathrm{A}\left(\frac{b}{2m}\sin\gamma-q\cos\gamma\right)=\frac{\mathrm{M}vgl^2}{96\mathrm{EI}}\left\{\frac{48\mathrm{EI}-32\mathrm{M}v^2l+5mv^2l^2}{8\mathrm{EI}+\pi\mathrm{M}v^2l}\right\}.$$

These two equations lead to A and γ, and one term of the summation suffices.

By using further terms of the summation agreement at other chosen points of the beam with the initial conditions may be secured, and a closely approximate result be obtained.

Multiple Loads.

18. When a number of separate loads (forces or masses) act upon the beam the differential equation representing the forced vibration contains sets of terms of the types already discussed for single loads, the particular forms involved depending on whether the position of x lies to one side or other of the various load positions. The application of the method of successive approximation proceeds in exactly the same way as before; and the integration constants are obtained by taking account of the end conditions and by observing that the beam is continuous at each of the load positions.

In obtaining the first approximation assistance may be obtained from the principle that the displacement at any point of the beam due to a number of forces acting together is equal to the sum of the displacements at that point due to the forces acting separately. It should be noted, however, that in proceeding to the second approximation we cannot in general employ this principle, for the force arising, for example, from the acceleration of a moving mass M depends not only on the magnitude of M but also on the differential coefficient of its total displacement.

The method already described for the solution of the differential equation of motion is, however, quite general for the problems here considered.

Massive uniform beam freely supported under action of a spring-borne mass moving uniformly along it, including damping.

19. It will be obvious that the method of successive approximation may be applied to more complicated problems, and with any specified terminal conditions, in which, however, the effect of certain terms on the exact result is small compared with that of the applied load.

As an example, we may refer briefly to the case of a spring-borne load moving with uniform velocity along a beam.

Let the beam be of uniform section, be heavy, horizontal, and supported freely at each end, and be subject to damping.

Let the spring-borne mass be represented by M, let μ be the number of units of force which compress the spring by one unit of length, and let b' be its coefficient of damping.

Let λ represent the length of the spring at the instant of time t when the load has reached the position x_0 on the beam, and let P be the force exerted by it on the beam at that instant.

Adopting the same notation for the beam as previously, its equation of motion is the same as that given at the beginning of paragraph 16 if P is substituted for

$$\mathrm{M}\left(g-\frac{d^2y_0}{dt^2}\right).$$

The equation of motion of the spring-borne mass is

$$\mathrm{M}\left(g+\frac{d^2\lambda}{dt^2}-\frac{d^2y_0}{dt^2}\right)+b'\left(\frac{d\lambda}{dt}-\frac{dy_0}{dt}\right)=\mathrm{P}.$$

Now $\mathrm{P}=\mu(\lambda_0-\lambda)$ if λ_0 is the length of the spring when unstressed. Hence

$$\mathrm{M}\frac{d^2\mathrm{P}}{dt^2}+b'\frac{d\mathrm{P}}{dt}+\mu\mathrm{P}=\mu\mathrm{M}\left(g-\frac{d^2y_0}{dt^2}\right)-\mu b'\frac{dy_0}{dt}$$

represents the motion of the mass.

In applying the method of successive approximation we may proceed as follows :—

From the latter equation omit the terms in $\frac{dy_0}{dt}$ and $\frac{d^2y_0}{dt^2}$ as a first approximation and we obtain an equation that is readily soluble.

This equation is

$$\mathrm{M}\frac{d^2\mathrm{P}}{dt^2}+b'\frac{d\mathrm{P}}{dt}+\mu\mathrm{P}=\mu\mathrm{M}g.$$

Its complete solution is

$$P = Mg + A'.e^{-\frac{b't}{2M}}.\sin\left\{t\frac{\sqrt{4\mu M - b'^2}}{2M} + \gamma'\right\},$$

where A' and γ' are arbitrary constants.

Now at $t=0$, $P=Mg$ and $\frac{dP}{dt}=0$ for steady initial conditions. Hence we require $A'=0$. Thus we have $P_1=Mg$ as a first approximation to the value of P.

Next substitute this value of P in the equation of motion of the beam and omit therefrom the damping and acceleration terms.

We find for y the value y_1 as in paragraph 16, which is a first approximation to the value of the particular integral for y.

We now write down the complementary function for the equation of motion of the beam, add y_1 to it and determine the values of the arbitrary constants from the initial conditions of horizontality and of rest of the beam. Let the result be Y_1. Then Y_1 is a first approximation to the complete solution of the equation of motion of the beam.

We thus know $(Y_1)_0$ or the value of Y_1 at the position x_0.

We now return to the equation of motion of the mass and find a second approximation to the value of P. We substitute for y_0 the value just obtained for $(Y_1)_0$ and solve for P, remembering that $x_0=l-vt$. We thus obtain a second approximation P_2 to the complete solution for P. The arbitrary constants are to be determined from the initial conditions, as before.

Now, in order to obtain a second approximation to the value of y, substitute P_2 for P and y_1 for y in the equation of motion of the beam, and thence obtain y_2, which is a second approximation to the value of the particular integral for y. By adding to y_2 the complementary function and suitably determining the arbitrary constants we obtain a second approximation to the complete solution of the equation.

Obviously we may proceed in this step by step manner to such further approximations as may be desired.

When the load has passed completely off the beam its free vibrations are represented by the complementary function, or solution of the equation in which the applied force is omitted. This result has been given in paragraph 17.

VII. *The Attachment of Electrons to Neutral Molecules.*

By Leonard B. Loeb*.

IN a recent issue of this Magazine, in an article entitled "The Capture of Electrons by Molecules," Professor V. A. Bailey (1) reports results on the formation of negative ions in ammonia which appear to differ radically from some earlier results obtained by Professor H. B. Wahlin (2). In discussing the discrepancy, Bailey attempts to discredit the work of Wahlin and the writer (3), quoting sections of some of the writer's articles (4,5) without the full context. In view of the fact that there appears to be a serious discrepancy between the two results, and since the criticisms are in a measure ill-founded and unjustified, it seems necessary to correct the erroneous impression given by Professor Bailey's statements.

In 1919, while studying the abnormally rapid increase of the mobility of the negative ion in air below 100 mm. pressure, as shown by the apparent discordant results of Wellisch (6) and Kovarick (7), the writer (8) concluded that qualitatively at least all the results could be explained by an ingenious theory proposed in 1915 by J. J. Thomson (9). This theory, contrary to the usual belief, assumed that an electron, in order to attach a molecule to form a negative ion, required on the average a certain number of impacts (n) with the neutral molecules before it struck one in such a condition that it was able to attach. The quantity n *for simplicity was assumed to be a constant* depending on the chemical nature of the gas only, and was conceived of as being a large quantity in air.

Now, the phenomena under consideration above were phenomena occurring largely in gases at higher pressures, that is, from 50 mm. to 760 mm. of mercury. In order to establish the theory quantitatively, experimental methods applicable to such pressures and low values of the ratio X/p (field-strength to pressure) had to be devised. The method adopted was the square wave-form alternating current method with photo-electrons liberated at one plate of a parallel plate condenser (10). It was shown that, using the *simplifying assumption* of a constant value of the constant of attachment n, a rigorous quantitative test of the theory should be possible by this means. The method, however, as do *all methods of obtaining the constant n*, or its reciprocal the probability of attachment P, contains as one of the important parameters the square of the electron mobility in the gas $(K')^2$. When the attempts were made to test the equation quantitatively, the electron mobility was not known in gases above 100 mm. pressure, and the writer was forced to make such measurements for the first time himself. This he succeeded in doing for three gases, N_2, H_2, and He (11), where electrons do not attach at all (*i.e.*, where $n=\infty$), using the Rutherford method with a sinusoidal high-frequency alternating potential. These results, while subject to considerable correction and to some error, are certainly good to better than 20 per cent., and are the only values available for the electron mobilities in this pressure range.

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* Communicated by the Author.

When it comes to the question of the study of electron mobilities in gases where electrons attach, it was possible at higher pressures to make measurements on only one gas, air, owing to the difficulties introduced by the formation of ions in large numbers (12). The writer and Wahlin were therefore forced to make the best estimates of K′ which they could. This they felt justified in doing because of the large range of variation of *n* with different substances experimentally observed; for it seemed that the results would at least be correct in order of magnitude, and an order of magnitude describing so vague a phenomenon as the "electric affinity" of a gas was better than nothing. Accordingly, in publication the writer and Wahlin carefully qualified their estimates of the relative attachment constants found for different gases as being *merely "order of magnitude values,"* and stated clearly that the difficulty lay in the unknown value of the electron mobility K′. The data still stand to-day as the *only data even in order of magnitude* bearing on this important electronic behaviour for any large range of substances.

Later, Bailey (13) applied a diffusion method to the study of attachment. This method was applicable to very much *lower pressures only* (upper limit 100 mm. of Hg). To these results Bailey could apply the equivalent of the values of the electron mobility K′, that is, the electron velocity values obtained by Townsend and himself (14). Bailey obtained approximately the same value of *n* at his lowest X/p in air as the writer had obtained at the very low values he had used. Bailey, however, found that *n* varied with the electron energy (*i.e.*, was not constant) increasing as the energy increased. These results the writer accepted at once as being highly significant. More recently, Dr. A. M. Cravath (15), in the writer's laboratory, has carried the low-pressure measurements in air and oxygen further, using a new electrical method. Cravath not only found the variation with energy, but has shown that, contrary to Bailey's belief, n in air also varies with the pressure, and after passing a minimum at 0·9 volt energy in air again increases.

It now appears that Bailey⁽¹⁾ has made some measurements in NH_3 at values of X/p greater than 8, in which he found n to be of the order of 10^5, while Wahlin⁽²⁾ at X/p below 0·1 had observed values of n for NH_3 as high as 10^8. The difference *appears* to be more than a discrepancy in order of magnitude. Bailey attempts to ascribe this discrepancy, among other things, to impurities in the gas in Wahlin's work, although Wahlin used a technique of careful fractionation of the NH_3 with liquid air-cooling, and did not resort to the drying of NH_3 with P_2O_5. This criticism seems particularly remarkable, because Wahlin's value of n was *greater* than Bailey's, which would indicate greater purity in Wahlin's gas than in Bailey's, instead of the reverse.

The real cause of the discrepancy is probably of an entirely different nature. It is unfortunate that lack of space did not permit Wahlin to publish his experimental data. The fact is that with an alternating current of square wave-form Wahlin was able to obtain (as an example chosen at random from Wahlin's data) 55 per cent. electronic carriers across a plate distance of 1·65 cm. with a period of alternation of ·00136 second at 750 mm. pressure of NH_3. Similar data can be taken from any of Wahlin's measurements for time-intervals from ·0068 second to ·00136 second, and pressures from 200 to 760 mm. of NH_3. In order to check Wahlin's results the writer recently prepared some NH_3, and at 400 mm., using polonium as an ionizing source with an auxiliary field of 20 volts/cm. and 1 cm. deep under a gauze, he was able to observe the dual mobility curves of the Wellisch type with 10 per cent. of free electrons. This test for slow attachment is even more severe than Wahlin's, and is in good qualitative agreement with that author's findings.

The fact, then, that electrons can cover considerable distances in NH_3 at 760 mm., at values of X/p from 0·1 down, without attaching indicates than n must be considerably greater for NH_3 than air, for which n is of the order of magnitude of 10^5 or more, according to Bailey. In air under similar conditions free electrons are not observed until pressures of the order of 80 mm. are reached.

When it comes to evaluating n quantitatively, one is again faced with the question of the proper choice of K' for this gas. This value is completely unknown in NH_3 above 100 mm.

and for low values of X/p. Wahlin chose the same method of estimating K′ for all his gases(2,3). To accomplish this he took the electron mobility in N_2 at 760 mm. pressure, and multiplied it by the ratio of the mobility of negative ions in NH_3 relative to those in N_2 which gave $K' = 1170$. This method the writer admitted to be crude(3,5). Until, however, the values of K′ are known, it is possibly as good as any other method in this region. At present, however, there is available a new method of estimating the electron mobilities in NH_3, namely, that made possible by Compton's(16) equation for electron mobilities. In the present test of Wahlin's results this value will be used.

To calculate n for NH_3, the equations applicable become more sensitive for values of d^2/V more nearly equal to KT than the values of the quantities given in the data above. The conditions chosen for the values of the quantities in the calculation of n by the rigorous attachment equation(10) based for simplicity on an assumption of the constancy of n, to wit

$$\frac{i}{i_0} = \frac{6{\cdot}8 \times 10^{-16}\, n(K')^2}{KT}\left[e^{-\frac{1{\cdot}47\times 10^{15}}{n(K')^2}\left(\frac{d^2}{V} - KT\right)} - e^{-\frac{1{\cdot}47\times 10^{15}}{n(K')^2}\left(\frac{d^2}{V}\right)}\right],$$

were as follows :—$p = 760$ mm.; $i/i_0 = 0{\cdot}63$ (fraction of carriers crossing plates); ion mobility $K = 0{\cdot}75$ cm./sec. per volt/cm.; time of alternation $T = {\cdot}0068$ sec.; $d^2 = 2{\cdot}72$; $V = 60$ volts. K′ from Compton's equation for NH_3 for $d = 1{\cdot}65$, and $V = 60$ was found to be 1390 cm./sec. per volt/cm. It is possible that K′ is higher. Putting these values into the equation for the attachment and solving for n graphically obtains $n = 7{\cdot}9 \times 10^7$, which is not far from Wahlin's value of 10^8.

Had the mobility K′ used been 2150 instead of 1390, the value of n would have been closely 10^7. Thus it is seen that the value of K′ enters into the determination in a very critical fashion. According as the value of K′ is chosen the value n obtained will vary widely. Now, Bailey(1) calculated n from his measurements, using values of K′ applicable to an $X/p = 8$ and more. The present results were obtained for values of $X/p = 0{\cdot}05$ and less, that is, the X/p differs in the two sets of measurements by a factor of about 160. In view of the fact that K′ and n both vary with X/p in an undetermined fashion, any comparison of the results of Bailey(1) and Wahlin(2) is meaningless at the present state of knowledge.

It accordingly appears that the criticisms of Bailey in regard to the pioneer work of Wahlin and the writer is both unnecessary and unjustified. The former because the writers had stated the limitations of, and assumptions involved in, their work as clearly as Bailey has, and the latter, inasmuch as the differences of the conditions underlying the two determinations preclude any comparison of values so that the differences observed in no sense reflect on the merit of either investigation.

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VIII. *The Energy of Hydration of Hydroxyl Ion and the Lattice Energies of Alkali Hydroxides. By* F. J. Garrick *.

THE energy of hydration of ions has been discussed by Fajans (1), Born (2), Latimer (3), and Webb (4), and values have been given by these authors for hydrogen ion, some metal kations, and halide anions. The data used include lattice energies and absolute electrode potentials. Corresponding to the lack of information regarding the lattice energies of hydroxides, the heat of hydration of hydroxl ion is not known.

In the present paper an attempt is made to find a value for this quantity, using various methods which lead to concordant results.

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* Communicated by Prof. R. Whytlaw-Gray.

The first method is based on a cycle and certain assumptions, and is independent of other ionic heats of hydration, lattice energies, and absolute potentials, while in the second the required value is obtained from the lattice energies of the alkali hydroxides. These are obtained by cycles, and in two cases also by another independent process, the values obtained by the two methods agreeing well.

1. *The Total Energy of Hydration of the Ions of Water.*

The following cycle is performed :—

$$\begin{tikzcd}
(H_2O)_{gas} \arrow[r, "II."] & (H^+ + OH^-)_{gas} \arrow[d, "III."] \\
Aq \arrow[u, "I."'] & (H^+Aq + OH^-Aq) \arrow[l, "IV."]
\end{tikzcd}$$

Stage I. consists in the evaporation of a mol of water. The water is ionized in Stage II. and the gaseous ions dissolved in water (Stage III.), and recombined in solution in Stage IV. The energy changes are as follows (denoting energy absorbed as negative) :—

Stage I. Heat of evaporation of water $= -L_{H_2O}$.
Stage II. Work of ionization of water vapour $= -D_{H_2O}$.
Stage III. Work of hydration of the ions $= W_{H^+} + W_{OH^-}$.
Stage IV. Heat of neutralization of strong acids and bases $= Q_{H_2O}$.

Then

$$W_{H^+} + W_{OH^-} = L_{H_2O} + D_{H_2O} - Q_{H_2O} \quad . \quad . \quad (1)$$

L_{H_2O} and Q_{H_2O} may be taken as 10 and 14 k.cal./mol respectively (5). For the value of D_{H_2O} two numbers are given. Hund (6) has given a theoretically calculated value of 370 k.cal./mol. Senftleben (7) gives 336 k.cal./mol. This value is based on observations which indicate that the energy corresponding to the resonance potential of mercury can dissociate water into H and OH. This energy, 112 k.cal./mol, is taken as being the upper limit for the heat of this dissociation. From this, by a cycle in which the electron affinity of OH is put equal to that of chlorine, the value of D_{H_2O} quoted above is derived. This value, then, so far as the experimental basis is concerned, is an upper limit, though the error in putting $E_{OH} = E_{Cl}$ might as easily give a low result as a high one. Recently, however, Gaviola and Wood (8) have shown that the value 112 k.cal./mol is not necessarily an upper limit, but the true value may be, and probably is, rather higher than this. It follows that D_{H_2O} is somewhat more than the value (336 k.cal. mol) given by Senftleben, and therefore it is reasonable to use the mean of this and the higher value of Hund, and so we have:

$$D_{H_2O} = 353 \text{ k.cal./mol},$$

and therefore, from (1),

$$W_{H^+} + W_{OH^-} = 349 \text{ k.cal./mol} \quad . \quad . \quad . \quad . \quad (2)$$

2. *Determination of the Individual Values.*

There is reason to believe that the "hydrogen ion in solution" exists as the ion H_3O^+, which appears to be a definite chemical individual (see, *e.g.*, Volmer, *Lieb. Ann.* cdxl, p. 200 (1924)). Also in this ion, and in other similar structures, it is generally held that the protons have penetrated into the interior of the electron structure of the oxide ion, so that these may be regarded as "pseudo-atoms" having an inert-gas structure (10).

On this view the ions H_3O^+ and OH^- would outwardly be very similar except in the sign of their charges. On this assumption we may consider that they have very nearly the same energy of hydration.

Now imagine Stage III. of the above cycle to be carried out as follows: evaporate another mol of water and combine this with H^+ to form gaseous H_3O^+. The energy evolved is $D_{H_3O^+} - L_{H_2O}$, where $D_{H_3O^+}$ is the heat of formation of H_3O^+ from a proton and water vapour. Now let the two complex ions H_3O^+ and OH^- dissolve in water. This whole process is considered to be equivalent to Stage III. above. Then we may write:

$$W_{H^+} + W_{OH^-} = 349 = W_{OH^-} + W_{H_3O^+} + D_{H_3O^+} - L_{H_2O}.$$

And since we assume $W_{OH^-} = W_{H_3O^+}$,

$$2W_{OH^-} = 349 - D_{H_3O^+} + L_{H_2O} \quad . \quad . \quad . \quad (3)$$

For $D_{H_3O^+}$ we have two estimates. Hund (*loc. cit.*) gives the theoretically calculated value $D_{H_3O^+} = 180$ k.cal./mol. Grimm (*loc. cit.*) (10), by assuming that the lattice energy of $OH_3 . Cl$ is equal to that of KCl, obtains $D_{H_3O^+} = 160$ k.cal./mol. As both of these values are rather uncertain, we again take the mean, and put $D_{H_3O^+} = 170$ k.cal./mol.

Then

$$2W_{OH^-} = 349 - 170 + 10 = 189 \text{ k.cal./mol}$$

$$\therefore \quad W_{OH^-} = 94 \text{ k.cal./mol.}$$

Combining this with (1),

$$W_{H^+}=349-94=255 \text{ k.cal./mol.}$$

This value agrees well with that of Fajans's ($W_{H^+}=262$) and that of Webb⁽⁴⁾ ($W_{H^+}=249{\cdot}6$).

(3) *Derivation of Lattice Energies of the Alkali Hydroxides and hence of W_{OH^-}.*

The following cycle is performed:—

$$\begin{tikzcd}
\begin{matrix}MCl_{cryst.}\\ +H_2O\end{matrix} \arrow[rr, "I."] & & \begin{matrix}(M^++Cl^-)_{gas}\\ +H_2O\end{matrix} \arrow[dr, "II."] & \\
 & & & \begin{pmatrix}M^++Cl^-\\ +H^++OH^-\end{pmatrix}_{gas.} \arrow[dl, "III."] \\
MOH_{cryst.}+HCl_{gas} \arrow[uu, "V."] \arrow[rr, "IV."'] & & (M^++OH^-+HCl)_{gas} &
\end{tikzcd}$$

Stage I. The solid chloride is coverted into gaseous ions, absorbing the lattice energy, U_{MCl}.

Stage II. The water is evaporated, and the vapour ionized. Energy change $=-L_{H_2O}-D_{H_2O}$.

Stage III. The H^+ and Cl^- ions form HCl gas evolving the energy, D_{HCl}.

Stage IV. The M^+ and OH^- ions condense to solid hydroxide, giving out the lattice energy, U_{MOH}.

Stage V. Solid hydroxide and HCl gas react to form solid chloride and liquid water, giving out the corresponding heat of formation of Q_{MCl}. Then (energy absorbed being $-^{ve}$),

$$-U_{MCl}-L_{H_2O}-D_{H_2O}+D_{HCl}-U_{MOH}+Q_{MCl}=O.$$

(For values see Table I.)

TABLE I.

$$\left.\begin{matrix}D_{H_2O}=353 \text{ k.cal./mol}\\ L_{H_2O}=\ \ 10 \text{ k.cal./mol}\end{matrix}\right\}\text{ as above.}$$
$$D_{HCl}=316 \text{ k.cal./mol}^{(11)}.$$

Metal.	$U_{MCl}^{(12)}$.	$Q_{MCl}^{(5)}$.	U_{MOH}.	
Na......	182	42	186	k.cal./mol.
K	162	47	161	,,
Rb.. ...	155	49	152	,,
Ca......	480	49	523	,,

Of course in the case of Ca the values of U and Q refer to one gm. atom of Ca, and we have in the equation (4) $2L_{H_2O}$, $2D_{H_2O}$, and $2D_{HCl}$.

The values of U_{NaOH} and U_{KOH} can also be obtained in another way. Hund (*loc. cit.*) gives a theoretically calculated value of D_{NaOH} and of D_{KOH}, the energies of dissociation of the vapour-molecules to gaseous ions. Obviously the sum of this value and the heat of sublimation is the lattice energy. Then, denoting the heat of sublimation by S, we have

$$U_{MOH} = S_{MOH} + D_{MOH}. \quad \text{(See Table II.)}$$

Table II.

Metal.	S_{MOH}(5)	D_{MOH}.	U_{MOH}.	
Na	31	150	181	k.cal./mol.
K	32	130	162	,,

A comparison of these values for U_{MOH} with those in Table I. shows that the agreement is very good, although Hund describes his values of D_{MOH} as uncertain.

These data may now be used to find W_{OH^-}, using the value of W_{M^+} given by Fajans and Born (*loc. cit.*) (1) and by Webb (*loc. cit.*) (4). Where their values differ, the mean is taken, the difference for the ions here considered never being greater than 4 k.cal./mol. Of course the sum of the ionic hydration energies is equal to the sum of the lattice energy and the heat of solution, or

$$W_{OH^-} = U_{MOH} + L_{MOH} - W_{M^+}. \quad \text{(See Table III.)}$$

Table III.

Hydroxide.	U_{MOH}.	L_{MOH}5.	W_{M^+}.	W_{OH^-}.	
NaOH	181†	10	101	90†	k.cal./mol.
	186*	10	101	95*	,,
KOH	162†	13	82	93†	,,
	161*	13	82	92*	,,
RbOH	152*	14	75	91*	,,
CaOH	523*	3	344	91*	,,

* From Table I. † From Table II.

4. *Discussion of Results.*

The values obtained by the various methods are very concordant, and the value of W_{H^+} obtained incidentally in section 2 agrees with those of other authors. A consideration of the way in which the chief possible errors are involved shows that the agreement can hardly be fortuitous. The most uncertain data used are those for D_{H_2O}, $D_{H_3O^+}$, D_{NaOH}, and D_{KOH}. Denoting the errors in these by ΔD_{H_2O}, $\Delta D_{H_3O^+}$, ΔD_{NaOH}, and ΔD_{KOH} respectively, we find that the value of W_{OH^-} derived in section 2 may have the error $\frac{1}{2}(\Delta D_{H_2O} - \Delta D_{H_3O^+})$, while of the values in Table III. those marked *, which depend on Table I., may have the error ΔD_{H_2O}, while those marked †, depending on Table II., may have the error ΔD_{NaOH} and ΔD_{KOH} respectively. Moreover, the value of W_{H^+} (section 2), which agrees with the results of Fajans and Born and of Webb (4), might involve the error $\frac{1}{2}(\Delta D_{H_2O} + \Delta D_{H_3O^+})$. Evidently a fortuitous compensation of errors can hardly have taken place.

We may therefore conclude with some confidence that (taking the mean) $W_{OH^-} = 92$ k.cal./mol. The concordance of the results may also be considered to support the assumption as to the similarity of H_3O^+ and OH^-, and the values of the lattice energies of alkali hydroxides given in Tables I. and II.

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IX. *The Nucleus as Radiator.* *By* W. M. Hicks, *F.R.S.*[*]

THE following considerations are offered in the hope of drawing attention to the nucleus of the atom as the essential origin of radiations. They are presented in a dogmatic form for the sake of clearness, but no dogmatism is intended. They are based on the assumption of the reality of the electromagnetic theory of light and the assumption that atoms are configurations of matter obeying the laws of dynamics and electromagnetism.

The Electron

(1) has inertia, and can possess momentum and energy of translation like a particle ;

(2) acts like a material particle charged with the negative electricity e ;

(3) when light, or an electromagnetic wave, passes across it, it is merely subject to the electric and magnetic forces in the wave-front.

In other words, the result is to subject it to small oscillations under the electric forces in the wave-front combined with small oscillating displacements perpendicular to the front, under the action of the magnetic force. No resultant forward mechanical impulse is imparted to it. The size of the electron is less than a millionth of a wave-length, and the analogy is with a splinter of wood floating on a long gentle swell. It is only when the swell strikes against, say, a sea-wall, that the wave-impulse produces a pressure effect. The light communicates no—or an infinitesimal fraction of its—impulse to the electron as it passes it. This seems clear if we follow dynamical reasoning. There is, also, no experimental evidence that such a transference of impulse ever occurs when a light-wave passes by a free electron. The electron when bound to a nucleus—at least as an outer valency one—is practically free, responding to the attractive forces of the nucleus and other electrons. The mutual distances are very large compared with their sizes, and again it follows that a train of light-waves cannot under any circumstances directly eject an electron from an atom.

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[*] Communicated by the Author.

The Atom.

We assume that an atom consists of a certain number of outside electrons (valency), a sheath containing only electrons, and a nucleus with a constitution cognizable by our finite minds, but at present unknown.

The Nucleus.

The nucleus is a complicated system involving + and − charges of whose configuration we at present know nothing. It settles the chemical nature of the atom and contains the machinery which, so to say, produces the characteristic reactions of the particular element. It can possess or store up varying quantities of energy. It can emit or absorb energy either by radiation or by ejecting electrons, or by rearranging its internal configuration. In radiation it follows quantum laws, that is, if it has a certain quantity of energy E to emit, it does so by radiations of frequency given by $h\nu = E$. It therefore takes a definite interval of time to do so. We might anticipate that some accident might prevent its continuation before the interval is completed, and the emission would apparently break Planck's law. In fact the energy to be emitted determines the frequency, and not the frequency the energy. On the contrary, in absorption the frequency of the incident light may determine whether it is absorbed or not by the nucleus, but the amount absorbed will depend only on the intensity and duration of the incident.

The free electrons seem never to fall into and neutralize the positive charges of the nucleus. We can explain this by postulating the existence of magnetic quality in the nucleus itself. Such magnetism must be of the nature of permanent magnets, or, if produced by the circulation of electric charges, their orbits must be constrained definitely to the nucleus itself, and not be orbitally free. In the latter case the orbits would be subject to great changes by electric or magnetic fields, and the nucleus itself be unaffected: the electrons could not transmit the forces on them to the heavy nucleus, but would simply modify their own motion. If an electron in an orbit round the nucleus were placed in a magnetic field, the well-known Larmor effect would take place, and the motion of the nucleus itself be unaffected. If, however, it moved in, say, a tube in the nucleus—or be fixed to a rotating nucleus—the latter would behave like a permanent magnet, setting its axis parallel to the field. Experiments on the lines of those of Stern and Gerlach can, therefore, give no information as to the arrangement of the orbital planes of the outer electrons of an atom. Probably the magnetic field at ordinary electron distances, say 10^{-8}, would be small, but at 10^{-10} it would be a million times larger—orbits closer in would be scrolls. If an electron began to fall straight into the nucleus in the equatorial plane of the magnet, it would describe scrolls round it and never reach it *. If, however, the line of fall were along the axis, the electron would ultimately reach the nucleus. Possibly, if its directions were slightly inclined, it might penetrate, but the proportion of incident electrons in general which could do so would be very small.

The outer electrons are merely the servants of the nucleus. The latter must be regarded as the source of any changes taking place, and under special conditions it is capable of ejecting electrons or of transferring them within the outer sheath. The relations are purely mechanical or electrodynamical, of whose nature we are at present completely ignorant. The only conditions we are to impose are that they must obey the ordinary dynamical laws.

In the emission of series lines and many related thereto, the frequencies are given by the difference of two terms, each of which is caculable from the energy in a special orbit. It is usual to regard the orbit as settling the terms, and many writers seem to consider that the electron itself radiates in changing its energy from one orbit to another. But while in transition its energy is altering, and the period is only determined when it arrives at the lower level. Rather we should regard the actual orbits as determined by the constitution of the nucleus, and that, while the orbits are changing, the excess energy is being continuously transferred to the nucleus, which stores and ultimately emits it with the proper frequency. That the special conditions are imposed by the nucleus would seem to be required also by the following considerations :—

(1) Where terms of the same k and different j exist, the j terms all depend on one of them—say p_1, p_2, p_3, on p_1—in a certain definite way by multiples of a unit, which for the same element depends with exactness on the atomic weight alone. It is difficult to see how the orbits could thus arrange themselves, except as fitting in with conditions imposed by the constitution of the nucleus itself—a constitution which settles the ratios of the numbers of its possible isotopes.

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* Proc. Roy. Soc. xc. p. 356 (1914) and xci. p. 273 (1915).

(2) All frequencies emitted by an atom, however, do not depend on the difference of two terms, but involve four or very many others (linked lines, etc.). Here the emitted energy cannot be produced by the transition of one electron from one orbit to another. Indeed, in many cases the number of terms is so large that there are not a sufficient number of outer electrons to produce them by simultaneous transitions. These lines are produced by more powerful excitations such as the spark, involving more intense electronic bombardment. We must suppose the excitation modifies the configuration of the sheath-electrons, or even that of the nucleus itself. It then emits, according to Planck's law, the total—or a portion—of that received from several subsiding excited electrons or displacements within it.

In the case of two-term emissions, we might perhaps regard the two particular orbits as producing some resonance or similar effect on the nucleus, causing the latter to so change its configuration that the reciprocal action causes the orbit to change, giving up energy to the nucleus, until the electron falls into a lower one, when again a resonance effect causes the nucleus to revert to its normal state, and the energy ceases to be transferred. This base-orbit must be completely stable, without the dissipation caused by the motion of exterior fields. Indeed, many phenomena seem to suggest that a base electron completely shields the nucleus in the same way as if its charge were uniformly distributed over a sphere round the nucleus, the latter behaving as if its charge were diminished by one e. Again all the actions must be dynamical. To see that such are possible we may take a purely supposititious model.

To fix ideas, take the case of a hydrogen-like atom with one electron revolving round a central nucleus. Let us define for the moment the action as the time-integral of the *kinetic* energy during a period. Let W be the energy-defect in the orbit, *i.e.*, the defect of the actual kinetic energy at any point below that produced by a fall from freedom. We can express this action by nh, where h is Planck's constant and n a pure number, not necessarily integral. Then the period of the orbit is given by ν, where $n_1h\nu_1=\mathrm{W}_1$. According to Planck we should get, therefore, in a transition,

$$n_1h\nu_1-n_2h\nu_2=\mathrm{W}_1-\mathrm{W}_1=mh\nu,$$

$$m\nu=n_1\nu_1-n_2\nu_2,$$

where m is integral. Following Bohr, it is usual to take $m=1$, but there seems no *à priori* reason why we should not find lines with other multiples[*]. The transformation here indicated, however, never takes place unless n_1, n_2 are themselves integers, that is, unless the orbital periods are themselves given by Planck's law. When this happens, let us imagine some resonance effect causes a rearrangement of magnets within the nucleus whereby the external magnetic field is increased; or say the nucleus becomes polarized to a dipole with an induced + charge fixed on it. In the first case the electron finds itself in a much stronger magnetic field, its path is bent by a force perpendicular to its direction of motion, and its angular momentum changes. The consequence is an equal and opposite reaction on the magnetic system of the nucleus, putting it in motion and producing a moving magnetic field at the electron, with consequent electric forces to diminish its energy, increasing that of the nucleus. On the second supposition, with the nucleus rotating more slowly than the electron, the electron is moving under a sort of tidal reaction (frictionless) until it reaches the opposite position, when the nucleus allows it to interchange the signs of the dipole, and so on.

It is possible that the nucleus is not capable of actually radiating unless it has received the energy to be radiated by a fall from one orbit to another. When it has absorbed energy in any way it may store it for a time, so that the emission does not take place immediately after the receipt of a given amount. It may thus receive many quota due to successive falls, then use the complete amount to raise an electron to a suitable level—one of its critical levels—and on the latter transiding in the normal way, the nucleus may emit the whole with the proper frequency. This would give an explanation of the existence of displaced and linked lines.

But if the nucleus is capable of using any excess energy in projecting a lower electron to run in some outer orbit, this will not in general be "quantized," *i.e.*, a critical level. It will be comparatively stable, losing energy continuously as an accelerated electric charge. In the course of this continuous fall it must change to one with the energy of a quantized orbit. Immediately (perhaps) it loses what stability it had[†], and begins to transfer its energy rapidly to the nucleus, and falls to its lowest level or another quantized orbit. If we could view the state of such a gas we should then see a considerable proportion of atoms with an outer electron circling at all kinds of distances. If these fell in, and their energies were radiated, the total light would be diffused over a continuous spectrum of very feeble intensity. But as they only fall in when they happen to reach a small number of particular states which enable the energy to be transferred, the total energy is radiated in a few frequencies only, and these are consequently more intense.

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[*] In fact I have unpublished examples of such.

[†] This is, of course, the exact opposite to the usual way of regarding the "quantized" orbit. But under that view it would seem indispensable to explain why a quantized orbit does not dissipate energy like an unquantized one.

Photoelectric Effect.

When a rapidly moving electron impinges on an atom, it is in general deflected without loss of energy, as if a perfectly elastic body. If, however, its energy is greater than a certain critical value E, depending on the nature of the atom, another electron is ejected, and the impinging one loses energy. The critical energy E measures that required to raise the ejected one from its lowest or base level, and free it from the nucleus. Later the nucleus captures another free electron, and then emits the excess energy by radiation of frequency given by $E=h\nu$.

Now consider what happens on our suppositions if light of frequency ν be incident on the nucleus. The nucleus absorbs it until it has received the quota $h\nu$. Before emitting it as light, however, it has to raise an electron to the proper level, and on the electron falling back the nucleus radiates the energy with frequency ν. If, however, the incident frequency is given by the above critical value, the valency electron is raised so far as to become free—or the electron is ejected. Later the nucleus captures another electron, and may radiate the equivalent ν. But meanwhile, apparently, the incident light has ejected an electron, whereas really the ejection is a secondary effect. If the incident light is of small intensity, the nucleus will have to wait longer to get its full quota, and a fewer number will be ejected per second.

The time taken by a nucleus to absorb a quota must be very considerable. Consider, for example, the light emitted from a single source, say one of 40,000 W.N. ($\lambda=2500$ A.) capable of showing interference due to path-difference of, say, $600{,}000\lambda$. This energy at any time is spread throughout a spherical shell of about 15 cm. thickness, and constantly increasing radius, unless focussed to a parallel or converging beam. It is only the small proportion falling on the nucleus during the passage of this 15 cm. which can be absorbed by it. A very large number of emitted radiations must then pass before the quota is made up. Precisely the similar effect follows on a projectile theory of transmission of light, though here the nucleus must wait a very considerable time before a projectile falls on it.

The explanation of the Raman effect would seem to be obvious. With the incident light of frequency ν the molecule—or possibly one of the atoms in the molecule—absorbs a portion until it obtains a quota $h\nu$. It then raises an electron to the proper level. But in the molecule the base-level of the atom does not exist, and consequently the electron falls to a new low level constituted by the molecule, which corresponds to an absorption level of that molecule. The emitted light has thus a frequency equal to the difference of the two.

A dynamical explanation of the Compton effect on the basis of the undulatory theory of light has recently been put forth by Raman [*].

X. *The Composition of* ϵ *Bronze.*

By W. Hume-Rothery, *M.A., Ph.D.* [†]

Introduction.

THE composition and structure of the phase in the copper-tin system usually denoted ϵ has aroused considerable interest from both the practical and theoretical points of view. Most of the earlier investigators considered the phase to be a definite compound Cu_3Sn of fixed composition. Isihara [‡], on the basis of electrical conductivity measurements, stated that the compound could dissolve excess of tin, but, as pointed out by Haughton [§], the rates of cooling used were too rapid to enable equilibrium to be attained. Broniewski and Hackiewitz [||] annealed a series of copper-tin alloys for prolonged periods, after which various physical properties were measured, and it was claimed that the thermoelectric power-composition curves indicated that the compound Cu_3Sn formed solid solutions to the extent of about one atomic per cent. on either side. Unfortunately no information was given as to the accuracy of the analytical work or other details in this investigation, and, as far as can be seen from the small diagrams reproduced, the curves for thermoelectric power were inconsistent with those for electrical conductivity. This work also indicated that the δ phase had the composition Cu_4Sn, whereas the crystal structure work of Bernal [*], which was supported by metallographic evidence, indicated that the true composition of the δ phase was 20·6 atomic per cent. tin, so that it appears that the work of Broniewski and Hackiewitz is uncertain to about one half an atomic per cent.

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[*] Indian Journ. Phys. iii. p. 357 (1929).

[†] Communicated by Dr. N. V. Sidgwick, F.R.S.

[‡] Isihara, Journ. Inst. Metals, xxxi. p. 315 (1924).

[§] Haughton, *loc. cit.* p. 347.

[||] Broniewski and Hackiewitz, *Compt. Rend.* xvi. p. 651 (1928).

The crystal structure of the ϵ phase [†] was investigated by Morris Jones and Evans [‡], who found a close-packed hexagonal structure, but were unable to deduce the exact positions of the atoms, and later a paper appeared by Bernal (*loc. cit.*), in which the structure was shown to be more complex, and it was stated that "the accepted composition [§] is probably correct, analysis of the actual crystals giving 25·2 atomic per cent. tin, which gives 16 molecules of Cu_3Sn per cell. Micrographical analysis, however, gives 24·3 atomic per cent., which agrees better with the formula $Cu_{50}Sn_{16}$." As this appeared to indicate that there was a conflict between the results of the X-ray and metallographic methods, the present work was undertaken to see if the discrepancy could be accounted for.

Experimental.

The alloys were made from the purest electrolytic copper obtainable from Messrs. Hopkin and Williams, and from the "Chempur" tin of Messrs. Capper, Pass & Co., Ltd., both metals being guaranteed to contain less than 0·05 per cent. impurity. The alloys were prepared by melting the metals under charcoal in a pure alundum crucible, the molten mixture being stirred with an alundum stirrer, after which the metal was cast into heavy copper moulds with $\frac{1}{4}$-inch and $\frac{3}{8}$-inch holes. By thus preparing a narrow ingot in a heavy mould of high thermal conductivity, very rapid cooling was obtained, and the structure was correspondingly fine.

For the annealing experiments the alloys were placed in sealed glass tubes, and at the end of the annealings the tubes were quenched in cold water. Owing to the fact that the solid solubility limits of ϵ bronze are practically unaffected by temperature, a very accurate temperature control during annealing was unnecessary, and at the lower temperatures the control was by hand, giving an accuracy of about 10° C., whilst at the higher temperatures use was made of a Foster Temperature Regulator, by means of which the temperature was kept within 1 per cent. of any temperature (measured in degrees centigrade).

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[*] Bernal, 'Nature,' cxxii. p. 54 (1928).

[†] It should be noted that Bernal denotes by η the phase which is here (and also by Westgren) called ϵ.

[‡] Morris Jones and Evans, Phil. Mag. iv. p. 1302 (1927).

[§] *i. e.* the composition Cu_3Sn.

The alloys were very brittle, and in some cases it was necessary to mount them in fusible metal in order to prevent the edges from breaking away when the specimens were ground down for microscopic investigation. The etching of alloys which were almost homogeneous was a matter of some difficulty. Where considerable quantities of a second constituent were present, satisfactory results could be obtained by etching with acid ferric chloride or by polish attack with a reagent recommended by Smith (Journ. Inst. Metals, Advance Copy, no. 476), composed of sulphuric and hydrochloric acids and potassium bichromate. But where the alloys were nearly homogeneous, and the second constituent was finely divided, these reagents caused uncertain staining, and the best results were finally obtained by using an alcoholic solution of picric acid or a mixture of this with Benedick's reagent (meta-nitro-benzoic acid in alcohol). These reagents stain the ϵ bronze phase a reddish brown, and leave both the δ and η phases white. When the alloys are almost homogeneous, great care is necessary in the microscopic work, since a hurried examination under low magnification may readily lead to the conclusion that the alloy is homogeneous, when traces of the second constituent are really present.

Analysis.

Owing to the small range of solid solubility in ϵ bronze, the accuracy of the analytical work was of great importance. When treated with hot or cold nitric acid the alloys tended to leave a passive residue which did not dissolve, but this difficulty was overcome by grinding the alloy to powder, and in the first series of analyses the tin was determined as dioxide in the usual way, but the results were uncertain owing to the well known adsorption of copper and to the tendency of the tin to go into colloidal solution ; the values thus obtained are entered in Table I. under the heading "crude tin-dioxide method."

A second series of alloys was analyzed electrolytically by the method recommended by Raper (Journ. Inst. Metals, xxxviii. p. 230, 1927), the alloy being dissolved in a mixture of nitric and sulphuric acids, the copper determined electrolytically, and the tin taken by difference. According to Raper (*loc. cit.*), this method is accurate to at least 0·1 per cent., and from Table I. it will be seen that in the six cases in which duplicate determinations were made the maximum difference is 0·1 per cent., and that in five out of the six cases the differences are not greater than 0·06 per cent. As a further check upon the accuracy of the analysis, alloys nos. 3, 5, and 7 were analyzed by a method in which the stannic oxide precipitate was purified by fusion with sulphur and sodium carbonate (see Treadwell and Hall, 'Quantitative Analysis,' p. 215). The differences between these values and those obtained electrolytically were ·01, ·22, and ·05 per cent. respectively, and in view of the well known difficulty in purifying a precipitate of stannic oxide—in general three successive fusions were necessary—the agreement is fairly satisfactory, and it seems probable that the electrolytic values can be depended on to about 0·1 per cent., and hence that the results can be expressed to within 0·1 atomic per cent., since in this region 0·1 per cent. by weight corresponds with ·07 atomic per cent. These results are summarized in Table I.

Table I.

No. of alloy.	Intended composition.	Composition by crude tin-dioxide method.	Composition by refined tin-dioxide method.	Composition by electrolysis.	Atomic per cent. tin.
1	37·1	37·0	—	37·14, 37·19	24·06
2	37·5	37·25	—	37·31	24·18
3	37·8	38·05	37·69	37·63, 37·73	24·47
4	38·1	37·81	—	38·14, 38·15	24·82
5	38·3	38·52	38·03	38·26, 38·23	24·93
6	38·5	38·88	—	38·32, 38·26	24·96
7	38·8	39·01	38·64	38·59, 38·59	25·18
8	39·1	38·86	—	38·80	25·34
9	39·4	39·47	—	39·36	25·80

Note.—The atomic percentages are calculated from the composition determined by the electrolytic method, taking the mean value if two determinations were made.

Equilibrium Conditions and Times of Annealing.

The equilibrium conditions of the copper-tin system are such that the ϵ phase is, on the copper side, in equilibrium with the δ phase up to 580°, and with the γ phase from 580° to 680°, at which temperature the ϵ phase decomposes. Since the composition of the γ phase is nearer to that of the ϵ phase than is that of the δ phase, alloys lying on the copper side of the ϵ phase show a much greater relative proportion of the second constituent above 580° than below this temperature. On the tin side the ϵ phase is in equilibrium with the η phase up to 415°, and then with liquid up to 625°, at which temperature the γ phase bends over and is in equilibrium with the ϵ on either side. In the cast state, however, all these alloys contain low melting constituents, and if a fine structure is to be obtained with specimens annealed above 415° it is essential that a preliminary annealing be given at low temperature. The actual times of the annealing experiments are given in Table II.

Table II.

1. 200° for 32 days and then quenched.
2. 300° for 28 days and slowly cooled.
3. 400° for 22 days and then quenched.
4. 500° for 14 days after 32 days at 200°; quenched from 500°.
5. 625° for 7 days after 28 days at 300°; quenched from 625°.
6. Alloys from (3) re-annealed at 200° for 7 days and quenched.
7. Alloys from (4) re-annealed at 175° for 7 days and quenched.
8. Alloys from (4) re-annealed at 300° for 7 days and quenched.

Experimental Results.

The experimental results can be considered most conveniently by describing the structures of the individual alloys, under the following headings :—

1. Alloys 24·06, 24·18, 25·34, and 25·80 * contained two constituents after all the conditions of annealing shown in Table II. In the case of alloys 24·06 and 24·18, the second constituent at temperatures between 175° and 625° was a solid phase, the γ phase at 625°, and the δ phase at lower temperatures. With alloys 25·34 and 25·80 the second constituent at 175°, 200°, 300°, and 400° was the solid phase η, whilst at 500° and 625° the quenched alloys contained crystals of ϵ surrounded by chilled liquid.

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* In this paper the system of Heycock and Neville is used, and an alloy described as, *e. g.*, alloy 24·5, means one containing 24·5 atomic per cent. tin.

2. Alloy 24·47 contained slight but definite traces of a second constituent under all conditions of annealing. There was a marked difference between the relative amounts of the second constituent in alloys 24·18 and 24·47, but the second constituent was always definitely present in the latter alloy, although in very small quantity, so that the composition is clearly very close to the boundary line of the solid solution, and we may therefore place this at approximately 24·5 atomic per cent. tin. The obtaining of this alloy was a fortunate coincidence, since it was clearly just on the boundary line.

3. Alloys 24·82, 24·93, and 24·96 were homogeneous after annealing and quenching from 400° and 500°, while at 625° C. alloys 24·82 and 24·93 were quite homogeneous, and alloy 24·96 may have contained traces of chilled liquid, but this could not be decided conclusively owing to the brittleness of the specimens. In the alloys annealed at 300° and then slowly cooled, alloys 24·93 and 24·96 were homogeneous, but alloy 24·82 contained slight traces of a second constituent. In order to see whether this was due to the fact that equilibrium had not really been reached, the whole series of alloys annealed and quenched from 500° was re-annealed at 300° for 7 days and quenched, when alloys 24·82, 24·93, and 24·96 were all homogeneous, showing that equilibrium had not been quite reached by the annealing at 300°; all other alloys were two-phase. These three alloys annealed at 200° for 32 days were nearly homogeneous, but definitely contained traces of a second constituent; but this again was because equilibrium had not really been obtained, for, in two separate series of experiments, alloys annealed at and quenched from 400° and 500° were re-annealed at 175° and 200°, but remained quite homogeneous, without precipitation of a second phase. These results indicate that a definite range of solid solubility exists.

4. Alloy 25·18, after all conditions of annealing and quenching, was definitely just outside the limits of the ϵ solid solution, the specimen quenched from 175°, 200°, 300°, and 400° containing traces of the η phase, whilst those quenched from 500° and 625° contained chilled liquid.

Discussion and Conclusions.

From the results of the present work it may be concluded that the ϵ bronze phase is a solid solution of which the limits vary from 24·5 to 25·1 atomic per cent. tin, any variation of the solid solubility with temperature being within the limits of the experimental methods. This range of compositions includes the simple whole number ratio Cu_3Sn, and is thus in agreement with the X-ray crystal analysis of Bernal to which reference has been made, but amplifies the metallographic investigation to which the latter referred. In a recent private communication Mr. Bernal has kindly told the author that at a later date he considered that his X-ray data might agree with the formula $Cu_{50}Sn_{16}$, but that as the positions of all the atoms had not been worked out, a definite conclusion could not be made, so that the X-ray data are not conclusive; but it is satisfactory to note that the present work is in agreement with Mr. Bernal's original conclusion, and that no conflict exists between the X-ray and metallographic results.

It is doubtful whether the microscopic method is accurate to more than 0·1 atomic per cent. with brittle compounds, so that it can hardly be said conclusively that the compound Cu_3Sn forms a solid solution with excess of tin, and it seems more than probable that the phase in equilibrium with the liquid is the pure compound Cu_3Sn. In this connexion it may be noted that the work of Matsuyama * indicates that the magnetic properties of molten copper-tin alloys show singularities in the neighbourhood of 25 atomic per cent. tin, indicating that a compound exists in the *liquid*, and hence, presumably, that there is a definite molecule of Cu_3Sn or some simple multiple of this formula.

On the other hand, the work seems to show conclusively that a solid solution exists on the copper side of the compound to an extent of about 0·5 atomic per cent., which is well outside the limits of experimental error. We seem, therefore, to have a real compound, in the chemist's sense of the word, corresponding to the existence of a definite molecule, but which can take up small amounts of one of its constituent elements into solid solution. It would be of great interest if a detailed examination of this very slight solid solution could be made by X-ray crystal analysis, since it is by no means clear that such a solution will be formed by the simple substitution process which is known to operate in the case of solid solutions of wide range. But if such an examination be made, the importance of a thorough annealing of the specimens cannot be overestimated, for it seems to be quite definitely established that in some alloy systems annealing may first produce a solid solution with the atoms arranged at random on a common lattice, whilst if the annealing be continued the atoms undergo further rearrangement, and in such cases it is clear that conflicting results will be obtained if the X-ray analysis be made before the final state is reached.

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* Matsuyama, Sci. Rep. Tohôku Imp. Univ. xvi. p. 447 (1927).

Acknowledgements.

The author must express his thanks to Professor W. H. Perkin, F.R.S., for having given laboratory accommodation for the present work, and to Sir Harold Hartley, F.R.S., for allowing the electrolytic analysis to be carried out in his laboratory. He must also acknowledge his indebtedness to Messrs. Brunner, Mond & Co. Ltd., for their assistance towards this and other research work, and to the President and Fellows of Magdalen College for a research grant.

Magdalen College, Oxford,
May 1929.

XI. *On Single Crystal Cathodes. By* K. G. Emeléus, *M.A., Ph.D., Lecturer in Physics, and* Jean W. Beck, *Queen's University of Belfast* *.

THE normal cathode fall in potential (V_n) of a glow-discharge has been found to be closely connected with the work function (ϕ) of the cathode for electrons. There is some evidence that in at least one instance the work function of a single crystal changes from one face to another $^{(1)}$, and it might therefore be anticipated that the discharge phenomena would be different if single crystal cathodes were used instead of ordinary polycrystalline pieces of metal. The fact that the latter present a mosaic of microcrystals to the ionized gas—unless they become fundamentally altered in their surface-layers under the influence of the discharge—might conceivably be responsible, through some averaging action, for the fundamental property of the normal discharge, viz., contraction of the discharging area at constant current density and constant cathode fall in potential (V_n) as the total current from the whole cathode is diminished. If this were so, a discharge should disappear from all parts of a surface of a single crystal simultaneously when the cathode fall reached its normal value. In addition, the value of V_n should vary from one face to another proportionately with ϕ. Up to the present, we have been unable to obtain suitable metallic crystals to enable us to examine these points. We have, however, investigated the discharge from a crystal of pyrites (FeS_2) in various gases, and have found that continuous contraction of the discharging area occurs with this at normal cathode fall, as with ordinary material. The measurements of V_n also permit an estimate to be made of the work function of pyrites, and give some indication of its chemical behaviour in the discharge.

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* Communicated by the Authors.

The crystal used was a cube, of side 1·4 cm. It had an electrical resistance of 62 ohms between opposite faces, but with the small currents that were passed through it in the discharge, of the order of 10^{-3} amp., the resulting fall in potential was almost negligible. The crystal was too hard to drill, and had to be supported by binding wire tightly round small notches in its edges. At intervals during the experiments the crystal was freed from possible impurities by lightly rubbing with emery paper; its behaviour was, in fact, unchanged by this treatment. All the main surfaces of this form of the crystal have identical surface lattices of atoms and behaved identically in the discharge.

The design of the discharge-tube used for the final measurements of V_n is shown in fig. 1. The whole of the crystal (C), except its lower face, was protected by a glass shield of square section. The anode (A) consisted of a cylinder built up of nickel and molybdenum wire, so that the cathode could be seen through it, and was degassed before mounting. The lower end of the tube was rounded off, and, whilst a discharge was passing, liquid air was kept round it up to the inlet-tube L. Pressures were measured by a McLeod gauge, without any allowance for fluctuations in temperature and density throughout the apparatus. The gases used were argon, freed from nitrogen by the calcium arc; nitrogen, prepared by exploding sodium azide (Kahlbaum), and stored over the resulting finely-divided sodium; oxygen, prepared by heating potassium permanganate (Kahlbaum); air, freed from carbon dioxide and water; and neon, containing some two per cent. of helium, but kept otherwise pure by means of charcoal cooled by liquid air. Before admitting each specimen of gas, the tube was baked, except for the part immediately adjacent to the crystal, and it was protected from tap-grease and mercury vapour by one or two liquid air-traps. On prolonged passage of the discharge the crystal tarnished somewhat in all the gases, but the effect was pronounced for short times of passage of the current for oxygen alone.

The procedure consisted in measuring the least potential at which the discharge would pass at different gas-pressures, using for this purpose a potentiometer (1300 ohms) with a maximum of 450 volts. A typical series of results is given in Table I. To obtain a closer approximation to the cathode fall in potential, these numbers should be diminished by the ionization potential of the gas when an anode glow is present (2); the corrected potential then becomes almost constant over a considerable range of pressures. There is

Fig. 1.

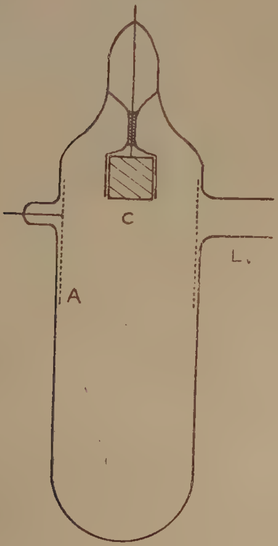

TABLE I.

Minimum glow-potential in oxygen at various pressures.

Glow-potential: volts	392	388	385	373	374	375	378	382	393	413
Pressure: mm. mercury	4·92	3·38	2·38	1·70	1·25	0·89	0·68	0·48	0·29	0·16
Anode glow ...	+	+	+	–	–	–	–	–	–	–

a slight tendency to increase at the higher pressures, probably due to an increase in the fall in potential in the non-luminous region between the negative glow, which was then closely contracted on to the cathode, and the anode glow. The more pronounced rise at lower pressures took place after the negative glow had expanded up to the anode, and is to be attributed partly to a true rise in the normal cathode fall (3), and partly to constriction of the discharge. The curve between pressure and minimum glow-potential is closely similar to that obtained when the minimum potential at which the discharge will run is measured for different positions of a movable anode (4), and the corrected applied potential, which is obtained immediately before the low-pressure rise, has been taken to be the normal cathode fall in potential.

The values of V_n obtained are collected in Table II. V_n' is Güntherschulze's value for the normal cathode fall in potential on an iron cathode at the pressure p at which the numbers against V_n were determined (3). Any error due to possible changes in the V's with pressure is only important in the case of nitrogen, and even then cannot be large. ρ is the ratio of V_n to V_n'. Accurate values of the thickness of the cathode dark space and of the normal current density could not be obtained with this apparatus, but they varied with pressure in the usual way.

Table II.

Normal cathode fall in potential in various gases.

Gas	Ar.	Ne.	N_2.	O_2.	Air.
V_n: volts	222	168	288	373	314
V_n': volts	168	153	215	352	337
p: mm. mercury	(1·0)	(2·0)	0·76	1·70	0·50
ρ	1·32	1·09	1·34	1·06	0·93

The numbers in brackets are rough estimates made from the appearance of the discharge; the gauge was not in connexion, to avoid as completely as possible the presence of mercury vapour.

The ratio ρ should measure approximately the ratio of the work functions for pyrites and for iron. Examination of Table II. shows that ρ is not far from unity for air and for oxygen; since the surface of an iron cathode is but little affected by a discharge through oxygen, this probably indicated that preferential oxidation and removal of sulphur were taking place. The value of V_n for neon was obtained from a single measurement in a quartz tube, under conditions in which there was a slight access of carbon vapours from some picein rimmed glass to quartz joints, and rather less efficient liquid air cooling than in the glass tube of fig. 1. In the quartz tube the ultra-violet spectrum of the negative glow, in addition to showing the majority of the lines of Ne I (5), Ne II, and Ne III (6), included well-developed bands of carbon monosulphide (7). The normal cathode fall in nitrogen was diminished by about 30 volts when liquid air was removed from the glass tube, so that it is probable that in the case of neon, when sulphur compounds were certainly present in the gas-phase, the value of V_n was also too small. V_n is also slightly less for neon when a little helium is present. It is concluded that the value of ρ for neon should be increased. The values of V_n for argon and nitrogen should be fairly reliable. Taking 1·3 as the most probable value of ρ, and 3·7 volts for the work function of iron, ϕ for pyrites is 4·8 volts. No direct determination of the work function of pyrites appears to have been made which could serve as a check upon this result, which is subject to all the uncertainties that arise in our measurements of V_n. These have been exaggerated by the use of a substance that is not an element as cathode, and we claim little more than to have pointed out the possible existence of a new effect in the normal discharge, and to have indicated an indirect method for obtaining the work functions for single crystals.

Summary.

A single crystal (pyrites) behaves like an ordinary piece of polycrystalline metal in the glow-discharge when used as a cathode. From the value of the normal cathode fall in potential in various gases, the work function of pyrites for electrons is calculated to be 4·8 volts.

We have to thank Prof. J. K. Charlesworth for providing the crystal, and for advising us on its structure.

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XII. *The Amount of Uniformly-diffused Light that will pass through Two Apertures in Series.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

SOME time ago I made some calculations about the stationary flow of very rarefied gases through capillary tubes [*]. In accordance with Knudsen [†] these calculations are based on the validity of the "cosine-law" for the reflexion of the gas molecules by the walls of the tubes. This law is essentially the same as Lambert's law in optics. Now, my attention has been drawn to an article of Dr. L. F. Richardson [‡] in the November number of the Philosophical Magazine. Dr. Richardson there calculates the amount of uniformly-diffused light that will go in series through two apertures forming opposite faces of a cube. He starts with the general integral

$$F=\iiiint \frac{\cos\zeta_1 \,.\, dA_1 \,.\, \cos\zeta_2 \,.\, dA_2}{r^2}, \quad . \quad . \quad (1)$$

in which dA_1, dA_2 are elements of the area of the apertures, r is the distance between the centres of dA_1, dA_2, and ζ_1, ζ_2 are the angles which the normals to dA_1, dA_2 make with the line joining the centre of dA_1 to that of dA_2. Coming to the special case of the cube, he derives an approximative value of F by replacing this integral by sums of respectively 1^4, 2^4, 3^4, and 4^4 terms and extrapolating to ∞^4 terms. In this way he obtains the value

$$F=(0{\cdot}6278\pm0{\cdot}0001)l^2, \quad . \quad . \quad . \quad . \quad (2)$$

in which l represents the length of the edge of the cube.

I wish to point out that this result may be obtained in a much more general form by direct integration of (1). Going back to my former publications, I found values of F for different forms of the apertures. Adding F for rectangular apertures and suppressing all values which may be easily derived from others, I obtain the following results:—

I assume that the apertures lie in two parallel planes, and that the line joining the centres is (1) a normal to these planes, and (2) the boundary of a movable plane which cuts the circumferences of the apertures in two corresponding points at a constant distance v apart.

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[*] P. Clausing, *Versl. Afd. Nat. Kon. Akad. Wet. Amst.* xxxv. p. 1023 (1926); 'Over den verblijftijd van moleculen en de strooming van zeer verdunde gassen,' Dissertation Leiden, Chapter iii. (Amsterdam, 1928).

[†] M. Knudsen, *Ann. d. Physik*, xxviii. pp. 75, 999 (1909).

[‡] L. F. Richardson, Phil. Mag. (7) vi. no. 39, p. 1019 (1928).

Two circles with radii r and r':

$$F=\frac{\pi^2}{2}\left\{2rr'-v\sqrt{v^2+4rr'}+v^2\right\}. \quad . \quad . \quad . \qquad (3)$$

Two equally orientated rectangles each with sides a and b:

$$\left.\begin{aligned}F={}&v^2\log_e\frac{(a^2+v^2)(b^2+v^2)}{v^2(a^2+b^2+v^2)}+2av\arcsin\frac{a}{\sqrt{a^2+v^2}}\\&+2bv\arcsin\frac{b}{\sqrt{b^2+v^2}}+2a\sqrt{b^2+v^2}\arctan\frac{a}{\sqrt{b^2+v^2}}\\&+2b\sqrt{a^2+v^2}\arctan\frac{b}{\sqrt{a^2+v^2}}-4av\arctan\frac{a}{v}\\&\qquad\qquad\qquad\qquad\qquad\qquad-4bv\arctan\frac{b}{v},\end{aligned}\right\}(4)$$

in which now v is also the distance between the two parallel planes.

Formula (4) gives for $a=b=v=l$

$$F=0{\cdot}6279\,l^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

in excellent agreement with the value (2) of Dr. Richardson *.

Confining oneself to the cases of two apertures of identical form, one may easily obtain F in the following way. Join the corresponding points of the circumferences of the apertures by straight lines, forming a cylindrical tube. Move the plane of an aperture parallel to itself over a little distance dv. The two positions of the plane intersect an elementary ring on the wall of the tube. Next move the second plane over a distance δv, giving a second ring. Now first calculate F for these two rings, which only demands a double integration. Then integrate twice from v to ∞, and the F for the two planes is obtained, as is easily seen.

Yours faithfully,
Dr. P. CLAUSING.

Natuurkundig Laboratorium der
N. V. Philip's Gloeilampenfabrieken,
Eindhoven (Holland),
19 December, 1928.

Note at the correction.—Prof. Milne's result (Phil. Mag. (7) vii. no. 42, p. 273 (1929)) agrees with (3) (formula (272) in my dissertation) whilst (4) gives for $a=b=v=1$ the result obtained by A. Gerschun (Phil. Mag. (7) vii. no. 42, p. 419 (1929)).

XIII. *The Corona Discharge in Neon.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

MR. PENNING, in a recent note (Phil. Mag., March 1928, p. 632) to your journal gives the result of a single experiment with a simplified apparatus, on the discharge in neon, between a wire and a cylinder. He remarks that his result differs from those which I obtained in the experiments described in my paper "The Corona Discharge in Helium and Neon" (Phil. Mag. v. no. 30, p. 721), and he concludes that the gas which I used was impure.

Mr. Penning finds that in neon at 40 mm. pressure the potential required to produce a discharge with the wire positively charged is greater than that with the wire negatively charged. He states that, after heating the electrodes and pumping out the apparatus, neon gas was admitted which was "*then* freed from traces of impurities by a glow discharge." This glow discharge was apparently passed between the wire and the cylinder. There is no mention of a spectroscopic method having been used to see whether the discharge introduces or removes impurities, but he assumes that this discharge removes impurities.

The changes in potentials which he finds are not inconsistent with the results which I obtained in the preliminary experiments which I made in order to remove impurities from the electrodes. My nickel apparatus was contained in a long quartz cylinder within which a space was left where an electrodeless discharge was produced, and the light from the discharge was examined spectroscopically. It was thus possible to observe directly the effect of the discharge between the electrodes on the purity of the gas. In all cases I admitted pure gas to the apparatus, and in the spectrum of the electrodeless discharge no lines due to impurity were found before a glow discharge was passed between the wire and the cylinder.

Before any measurements of potentials were made, the apparatus was heated and washed out with pure gas. Also large currents were passed in both directions between the wire and the cylinder. This was found to be very effective in driving impurities from the electrodes, as was seen from the spectrum of the electrodeless discharge. This process was repeated many times, and eventually a state was reached when slight heating of the apparatus or the passage of a small current between the wire and the cylinder had no effect either on the spectrum of the electrodeless discharge or on the potentials required to maintain the currents.

It was found in the course of the experiments that the potentials required to maintain positive currents between the wire and the cylinder were increased when the gas became impure. The final results obtained with two different wires were in complete agreement, and were frequently repeated.

In the preliminary experiments before the apparatus was thoroughly washed out, the difference between the potentials required to start the positive and negative discharges was much less than that indicated by the potentials given in my paper. These preliminary experiments appear to be more consistent with Mr. Penning's observations.

On no occasion was it found possible to purify gas merely by the passage either of a direct or of a high-frequency discharge between the wire and the cylinder, or in similar experiments between parallel-plate electrodes.

Small traces of impurity may be removed from gas contained in a quartz or glass tube by an electrodeless discharge*, but this method of purifying a gas is not effective in removing large quantities of impurities which appear in the gas due to discharges between electrodes.

It would appear that in Mr. Penning's experiments impurities would tend to collect in the apparatus, and it would be impossible to estimate what effect they may have on the potentials required to produce discharges.

Yours faithfully,
L. G. H. Huxley.

The Electrical Laboratory,
Oxford.

XIV. *Notices respecting New Books.*

Flame and Combustion in Gases. By W. A. Bone, F.R.S., and D. T. A. Townend. (Longmans, Green & Co., Ltd., 39 Paternoster Row, London, E.C. 4.) Price 32*s.* net.

THIS volume, dedicated to Prof. H. B. Dixon, the "founder and doyen of the Manchester School of Combustion Research," covers the wide field of research on Flame and Combustion in Gases, especially the remarkable results obtained in France and England during the last forty or fifty years. The authors give a detailed account of recent progress in this subject, not the least important the noteworthy researches carried out in the Imperial College by Prof. Bone and his co-workers.

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* J. S. Townsend and S. P. MacCallum, Phil. Mag. (April 1928, p. 695).

With the exception of the historical review in the first chapter, the sections of the book on the initiation and development of flame and detonation in gaseous explosions, gaseous explosions in closed vessels, the mechanism of gaseous combustion and catalytic and incandescent surface combustion include a great part of Prof. Bone's researches, particularly the study of the combustion of mixtures of gases with oxygen and diluent gases under large initial pressures.

A very complete bibliography, setting out the names of authors and the titles of memoirs, is given at the end of each section. A number of beautiful plates, many from Prof. Bone's research records, photographs of flame movements, detonation waves and flame spectra, form a notable feature of this volume. Although almost daily advances are being made in the study of gaseous combustion, influenced to an increasing extent by the new ideas of atomic structure and radiation, 'Flame and Combustion in Gases' will long be recognized as the standard work on this branch of chemical science.

Matter, Electricity, Energy. By Prof. WALTER GERLACH. Translated from the second German edition by Dr. F. T. FUCHS. (Chapman & Hall, Ltd., 11 Henrietta Street, London, W.C. 2.) Price 30*s*. net.

As the sub-title indicates, this work deals especially with the experimental results of atomic investigation, and is intended to meet the needs of advanced students of physics and other related subjects. Prof. Gerlach's researches in many branches of modern physics are well known, in particular the Gerlach-Stern experiment, described in some detail in the chapter on the magneton. In each chapter the author discusses a particular topic from the experimental side, and presents a review of recent investigations in a clear and readable form. The periodic system of the elements, isotopy, electron charge, photoelectric and Compton effects, X-ray spectra and super-conductivity, and other important phases of modern physics, have been chosen for discussion.

Dr. Fuchs has carried out his task of translation in a commendable manner, and helped the author in his desire to rouse the interest of the reader and to ground him in the modern views of matter, electricity, and energy.

Probability and its Engineering Uses. By THORNTON C. FRY, Ph.D. [Pp. xiv + 476, with 49 figures.] (London: Macmillan & Co. 1928. Price 30*s*. net.)

THIS volume can be recommended without hesitation as one of the best introductions to the subject of probability. The treatment of the subject is clear and logical, and difficulties are carefully explained. No extensive mathematical knowledge is assumed, and where mathematics is introduced any step which might prove a stumbling-block to a reader with slender mathematical equipment is explained in a footnote. The theory is illustrated by numerous examples, including many of the classical problems, worked out in detail. Additional examples to be solved by the reader are given. It is to be regretted that the answers to these are not included: the student has not the satisfaction of knowing whether his solution is the correct one.

It might be inferred from the title that the volume is suitable for engineering students only. Such is not the case. The engineering applications form only a small portion of the volume, and are in themselves of great interest; the chapter, for instance, dealing with the theory of probability as applied to problems of congestion is concerned with problems connected with automatic telephone exchanges. Such problems form excellent illustrations of the theory, and can be read with interest by any student, no engineering or technical knowledge being required.

The subjects dealt with include Bernouilli's and Bayes's theorems; distribution functions of various types; averages; curve-fitting, including tests of goodness of fit and fluctuation phenomena.

In a series of appendices are given valuable numerical data and tables, including factorials, logarithms of factorials, binomial coefficients; the normal error function; the normal law, its integral and derivatives up to the sixth; Poisson's formula; Pearson's criterion of goodness of fit.

The Physics of Crystals. By Dr. ABRAM F. JOFFÉ. Edited by Prof. LEONARD B. LOEB. [Pp. xi+198, with 61 figures.] (New York: McGraw-Hill Book Co., Inc.; London: McGraw-Hill Publishing Co., Ltd. 1928. Price 15*s*. net.)

AN invitation to give a course of lectures in the University of California afforded Prof. Joffé an opportunity to collect together the results of a series of investigations, extending over twenty-five years, on the physics of crystals carried on by himself and his collaborators. The various problems brought under investigation are all discussed from the point of view of the electrical lattice theory of crystals.

The first six lectures are devoted to the elastic properties of crystals, and it is shown how these investigations checked the electrical theory not only qualitatively, but also quantitatively. By a series of well-devised experiments, involving a high degree of experimental technique, it is shown in a graphic manner how the various apparent contradictions to the theory were proved to be due to disturbing phenomena, such as the irregularities of heterogeneous bodies, interactions between crystalline grains, or rupture inside small weak spaces within the body. The author and his collaborators were enabled, by investigating the phenomena which limited the scope of an experiment, to extend their experiments far beyond the limit of previous studies. They found it possible, for instance, that the scope of the elastic forces studied could be extended about five hundred times beyond the usual limit of rupture. Similarly, in the investigation of electrical properties, they found that in sufficiently thin sheets electric fields could be attained which reached three hundred times the value usually producing electrical breakdown.

The last eleven lectures deal with the electrical properties of both single crystals and solid dielectrics. Many new problems are suggested by the experiments described, and some of these are now under investigation.

It should be emphasized that the volume deals with only that portion of the field of the elastic and electrical properties of solids which has been investigated by Dr. Joffé and his colleagues. The title of the volume is therefore somewhat misleading. The original publication of much of the work described was in Russian, and this book will make these researches available to a wider circle of readers. The author hopes that his further experiments may throw some new light upon the origin and laws of the repelling forces between the atoms in solids.

The Symmetrical Optical System. By G. C. STEWARD, M.A., D.Sc. (Cambridge Tracts in Mathematics and Mathematical Physics, No. 25) [Pp. viii+102, with figures.] (Cambridge: At the University Press. 1927. Price 7*s.* 6*d.* net.)

THIS is the second of the series of Cambridge Tracts in Mathematics and Mathematical Physics to deal with the symmetrical optical system. The tract under review is more advanced than the earlier tract by Dr. Leathem. It is essentially an exposition of the applications of the characteristic function of Hamilton or the allied function, the eikonal, to the theory of the symmetrical optical system, both from the purely geometrical and from the physical point of view. The various aberrations of optical systems are treated in some detail, and their geometrical meanings are explained. The diffraction patterns obtained with various shapes of aperture are investigated, and an account is given of the modifications of these due to the geometrical aberrations. One chapter is somewhat inappropriately named "The Computation of Optical Systems"; it would not be found of much assistance to the practical computer, although of theoretical interest. The mathematical treatment is somewhat compressed, and may offer difficulty to the reader of average mathematical attainments.

XV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. vii. p. 1206.]

April 24th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

'The Geology of Part of North-Western Rhodesia.' By Robert Murray-Hughes, F.G.S., Assoc.I.M.M.

After defining the scope of the work, this paper goes on to describe the physical geography of the area, which lies approximately between lat. 14° and 17° S. and long. 24° and 30° E. The subject falls into three natural divisions, which follow each other roughly from west to east. The first is the flat, somewhat swampy country overlaid by the Karroo and Kalahari rocks; the second is the old peneplain-surface forming the plateau of Northern Rhodesia and underlaid by the Transvaal and Pretoria rocks, and those of the Swaziland System; and the third, a deeply dissected country overlaid mostly by the Swaziland rocks and drained by the Zambesi and Luangwa rivers.

The Swaziland rocks, composed of gneiss, chlorite-schists, and kyanite-schists with various hornblendic rocks, are described, and a short description is given of the Old Granite intrusive, and of the more recent dolerites. It is suggested that the last-named are of Karroo Age.

The following groups, named the Lusaka and Kafue Beds, and formed of calcareous, dolomitic, and quartzose rocks, are described, and a tentative correlation of them is made with the Transvaal and Pretoria Systems of the south. The Hook Granite forms one of the most important features in the geology of the country, and is shown to be intrusive into the Lusaka and Kafue Beds, which are strongly metamorphosed by it. It is normally a biotite-granite; but, in contact with the older sedimentaries, it takes on the form of syenite, gabbro, hornblendite, etc. Dykes of quartz-porphyry and minette are the later manifestations of this intrusion.

The discovery of flat-lying grits and sandstones in the west are correlated with similar beds found in the Luangwa Valley, and those in turn with the Karroo Beds described and mapped by A. J. C. Molyneux in the south-eastern portion of the area.

The covering of sand in the west, together with certain 'ancient laterites', is correlated with the Kalahari System.

A short attempt is made to indicate the principal structural features, these being divided into four groups :—

(1) The north-east and south-west foliation caused by the intrusion of the Older Granites.

(2) The north-west and south-east fracturing caused by the intrusion of the Hook Granite.

(3) The graben faulting, which forms a part of the Great Rift Valley.

(4) The folding of the Karroo Beds.

A few of the more important thermal springs are described, the widespread occurrence of laterite and its mode of development is indicated, and the paper concludes with a few brief remarks on the belts of alluvium.

May 8th, 1929.—Prof. J. W. Gregory, L.L.D., D.Sc., F.R.S., President, in the Chair.

The following communication was read :—

1. 'The Glaciation of Eastern Edenside, the Alston Block, and the Carlisle Plain.' By Frederick Murray Trotter, M.Sc., F.G.S.

Three glaciations separated by intervals within the glaciation have been recognized in Edenside.

The ice of the First or Scottish Glaciation deployed from the Southern Uplands, swept across the Carlisle Plain, one stream continuing eastwards, the other advancing up Edenside (where it was joined by a stream from the Lake District) in a manner similar to that described by J. G. Goodchild. Exposures of the ground-moraine of this glaciation are rare, and in Eastern Edenside the moraine is in places overlaid by a series of contorted laminated clays, etc., which are interpreted as indicating the departure of the ice from Edenside. These clays are in turn overlaid by the drifts of the Second or Main Glaciation. During that period Eastern Edenside was occupied by Lake-District ice and Cross-Fell ice. Because of the presence of Scottish ice on the north and ice from Howgill and Wild Boar Fells on the south, Edenside became congested with ice. The surface-level of the ice rose to 2200 feet at least, and probably higher. An ice-shed was established in Eastern Edenside and on the Alston Block, and from it ice flowed south-eastwards into the Stainmoor depression and northwards and north-westwards into the Tyne Gap area. Thus the Stainmore Glacier was fed from the north by ice from Edenside and Mickle Fell, and farther east was joined by a stream from Upper Teesdale (as proved by Dr. A. R. Dwerryhouse). The glacier in the Tyne Gap was fed by a powerful stream flowing down Edenside, and by glaciers in the valleys of the South Tyne, West Allendale, and East Allendale. On the north the Tyne Gap Glacier was confluent with eastward flowing Galloway ice.

The retreat of the ice-front after the maximum of the Main Glaciation can be traced stage by stage, the following being the chief events in chronological order:—(1) Successive splitting-off, from east to west, of the East Allendale, West Allendale, and South Tyne glaciers from the ice in the Tyne Gap area; (2) Damming-up of glacier-lakes along the western slopes of the northern end of the Cross-Fell escarpment, and along the western slopes of the Bewcastle Fells, the drainage of both systems escaping into the Tyne; (3) Recession of the Edenside Glacier from the Galloway ice; and (4) Recession of the Cross-Fell ice from the Lake-District ice by successive splitting-off, from north to south, of six valley-glaciers of the Cross-Fell Inlier.

Several åsar-trains and kame-belts are recognized in the extensive deposits of outwash sand and gravel; of these the most noteworthy are the Tyne Gap åsar-train, which stretches westwards from Hexham for 26 miles, and the Brampton kame-belt, which is 12 miles long and 2 to 4 miles wide. It is shown that the outwash can be interpreted in terms of åsar, kames, outwash-fans, and outwash deltas, and by their aid and that of overflow-channels it has been possible to plot the position of the ice-front at twenty-four distinct halt-stages in the retreat.

The last glaciation of the area was the renewed advance of the Scottish ice across the Carlisle Plain, up to an altitude of 400 or 500 feet O.D. At its maximum extension, and during its retreat, this glacier dammed up glacier-lakes which drained south-westwards. Englacial or sub-glacial rivers of this glacier deposited three åsar-trains.

May 29th, 1929.—Prof. J. W. Gregory, LL.D., D.Sc., F.R.S., President, in the Chair.

The following communication was read:—

'The Pliocene and Pleistocene Deposits of Wadi Qena and of the Nile Valley between Luxor and Assiut (Qau).' By Kenneth Stuart Sandford, M.A., Ph.D., F.G.S.

Wadi Qena is a broad and deep valley which joins the Nile from the north at Qena, about 40 miles north of Luxor. The history of the two valleys is closely associated, and the former explains some of the problems of the latter. Like all the tributaries of the Nile (north of the Atbara), Wadi Qena is now a dry valley and a desert.

The oldest beds visible within the walls of the valley-system are of Pliocene age, deposited in a gulf of the Mediterranean. This had been cut by river-erosion during the elevation of the Egyptian plateaux in Miocene and (in the south) partly in Oligocene times, and it was then flooded to a height of at least 550 feet above present sea-level. A non-fossiliferous series of strata was deposited in it: breccia and conglomerate at the valley-sides interdigitating with limestones, which, towards the centre, give place to clays and marls and, rarely, to sandy beds of quartz derived from the south. Great thicknesses of travertine are locally present in the series.

Re-elevation carried tbe flooded valley-system back to fluviatile conditions in Plio-Pleistocene times, accompanied by the irruption of enormous quantities of detritus from the Red Sea Hills. Some interesting relics of this early invasion are to be found throughout the area.

In Pleistocene times an ordered succession of river-terraces was laid down in the Nile valley and in all the major wadis, and by countless short tributaries rising in the Pliocene deposits which lined the sides of those valleys. A complicated series of local and non-local stages results, in which the meanders of the Nile (in particular) and their effects on the local stages may be traced. The gravels of each stage contain Palæolithic instruments, and on the surface of each may be found the working-floors of the next succeeding industry. The sequence is:—

100-foot terrace: Chellean.
50-foot terrace: Acheulean.
30-foot terrace: Early Mousterian.
15-foot terrace: Mousterian.

Thereafter (in Upper Palæolithic times) desert conditions began to assert themselves, and the Nile alone survived, supplied from more favoured regions farther south.

At about the same time the Nile carved a deep channel of which we do not know the depth; it re-excavated the deeper parts of the Pliocene-filled Miocene gorge. The process of filling this up still continues.

There is good reason to suppose that certain fossil-bones found at Qau were derived from these now-hidden alluvial deposits. The fauna which they represent was not yet of desert type, and at the moment it can only be stated broadly, on external as well as on first-hand evidence, to be of Upper Palæolithic age.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]